Toluene Removal from Produced Water by Biofilm Granular Activated Carbon System

By

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Abstract

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Over the last several decades, new strategies for oil and gas produced water disposal have been explored due to concern over increasing seismicity in areas surrounding deep well injection sites. A large area of research is focused on treating produced water for disposal or beneficial reuse. A major constituent in produced water is aromatic hydrocarbons which have high chemical stability and are resistant to conventional biological treatment. The objective of this study was to investigate the ability of a system utilizing biofilm growth on granular activated carbon (BIO-GAC) to remove toluene, an aromatic hydrocarbon common in produced water. Two lab-scale upflow anaerobic sludge bed (UASB) reactors were operated in three experimental phases. A BIO-GAC reactor was inoculated with granular seed sludge from a UASB reactor at the Cedar Rapids, IA Water Pollution Control Facility and Filtrasorb 400 GAC from Calgon Carbon Co., PA. A biological (BIO) reactor was fed with the same granular seed sludge only with no GAC addition and was used as a control for experimentation.

In phase I, the BIO-GAC and BIO reactors were fed with synthetic produced water to simulate real characteristics found in produced water across the United States. Operational conditions were identical for each reactor. The hydraulic residence time was 10 days, and a recirculation pump was used to achieve an upflow velocity of 1.25 m/h at which the sludge bed

remained immobile at the bottom of the reactor. After 150 days of acclimation, both reactors had achieved COD removal rates around 80%. During this time, biofilm attachment on GAC particles in the BIO-GAC reactor was confirmed by scanning electron microscopy (SEM) imaging.

Phase II involved adding toluene at a level consistent with average concentrations in produced water, 10 mg/L, to the feed water. Analysis by solid phase micro-extraction (SPME) and gas chromatography (GC) found >99.9% toluene removal in all BIO-GAC effluent samples and an average 73.2±8.1% removal in the BIO reactor through 60 days. These results show significant difference between the two systems' toluene removal abilities, with BIO-GAC clearly superior.

The objective of phase III was to observe the effects of salinity on the performance of both reactors. Salinity started at 1% (10 g/L) in the influent feed and was subsequently increased by 1% every 7 days until a final level of 3%. Toluene removal rates in the BIO-GAC reactor remained steady at >99.9% throughout this phase. The BIO reactor, on the other hand, saw toluene removal of 85.5±2.8%, 64.2±7.0%, and 35.1±25.4% at 1%, 2%, and 3% salinity, respectively, displaying a clear decrease in performance. These results indicate salinity affected toluene removal performance in the BIO reactor, but also indicate the BIO-GAC reactor had a resistance to saline shock.

The findings of this study demonstrate BIO-GAC's ability to effectively treat produced water with high levels of toluene, even in hypersaline conditions. Moreover, removal rates of chemical oxygen demand (COD) remained steady at 80% throughout experimentation, indicating BIO-GAC systems have the ability to remove a wide range of constituents from produced water that would not be possible by BIO or GAC alone. Overall, the hybrid BIO-GAC system may be a

solution to the produced water disposal problem by presenting a treatment process that can be easily adopted by professionals in the industry.

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Abbreviations and Symbols

AWQC	- ambient water quality criterion
BIO	- biological
BIO-GAC	- biofilm on granular activated carbon system
BOD	- biological oxygen demand
BTEX	- benzene, toluene, ethyl-benzene, and xylenes
CAR	- Carboxen
CAS	- conventional activated sludge
Cc	- cubic centimeter
cm	- centimeter
COD	- chemical oxygen demand
CWA	- Clean Water Act
DBP	- disinfection byproduct
DNA	- deoxyribonucleic acid
DOC	- dissolved organic carbon
DOM	- dissolved organic matter
ED	- electrodialysis

EHS - Environment, Health & Safety

EPA - United States Environmental Protection Agency

ESS - effluent suspended solids

EVSS - effluent volatile suspended solids

FO - forward osmosis

g - gram

GAC - granular activated carbon

GC - gas chromatography

h - hour

HRT - hydraulic residence time

ID - internal diameter

KCC - Kansas Corporation Commission

KU - University of Kansas

L - liter

m - meter

MAI - microscopy and analytical imaging

MBR - membrane bioreactor

MCL - maximum contaminant level

MDL - method detection limit

MF - microfiltration

mg - milligram

mL - milliliter

MLVSS - mixed liquor volatile suspended solids

mm - millimeter

MS - mass spectrometer

ND - non-detect

NF - nanofiltration

NORM - naturally occurring radioactive material

NPDES - National Pollutant Discharge Elimination System

O&M - operation and maintenance

PAC - powdered activated carbon

pCi - picocurie

PDMS - polydimethylsiloxane

POTW - publicly owned treatment work

RO - reverse osmosis

rpm - revolutions per minute

SBR - sequencing batch reactor

SDWA - Safe Drinking Water Act

SEM - scanning electron microscopy

SIM - selected ion monitoring

SPME - solid phase micro-extraction

TDS - total dissolved solids

TOC - total organic carbon

TSS - total suspended solids

UASB - upflow anaerobic sludge bed

UF - ultrafiltration

UIC - underground injection control

US - United States

UV - ultraviolet

ZLD - zero liquid discharge

µg - microgram

μm	- micrometer
°C	- degrees Celsius

1.0 Introduction

Produced water is defined as a combination of two water sources: flowback water consisting of hydraulic fracturing injection fluids that return to the surface and formation water that is released from the fractured formation after hydraulic fracturing. Its composition is highly variable and depends on the characteristics of the geological formation from which it is produced (Li 2013). Produced water is the largest byproduct of oil and gas production. On average, approximately seven to ten times more water is produced than oil and gas (Guerra et al. 2011). Billions of barrels of produced water are generated in the United States annually (Veil et al. 2004). Discharging produced water can pollute air, water, and soil and cause seismicity issues as evident in the central United States (Fakhru'l-Razi et al. 2009, Bergman 2014, Jamaly et al. 2015). Due to increasing volumes, the disposal of produced water has become a critical environmental issue, prompting research aimed at optimizing treatment methods to meet water quality regulations for discharge and beneficial reuse.

Produced water in the United States generally consists of high organic content as well as recalcitrant and toxic dissolved organic matter (DOM) (Benko et al. 2008). Geological location has a significant impact on produced water characteristics including total suspended solids (TSS), salinity, naturally occurring radioactive material (NORM), and pH (Alley et al. 2011, Guerra et al. 2011). The diverse landscape of the United States creates a high variability in produced water composition across the country. One of the most commonly found contaminants in produced water is aromatic hydrocarbons. These compounds, which include benzene, toluene, ethyl-benzene and xylenes (BTEX), are volatile and extremely toxic to humans (Utvik 1999). Biological treatment has been shown to be a promising strategy for general produced water treatment in various studies

(Woolard et al. 1995, Sharghi et al. 2014). However, BTEX like all aromatic compounds are kinetically resistant to biodegradation due to the large energy required to break their stable ring-like structure (Weelink et al. 2010). Optimizing an effective treatment solution for BTEX removal is therefore a priority of produced water treatment.

A combination of biological and physical treatment that utilizes biofilm growth on granular activated carbon (BIO-GAC) has advantages for removal of BTEX in addition to other produced water contaminants. GAC is an effective adsorbent for a wide range of organic compounds due to its high porosity and large surface area (Radovic et al. 1997). In these BIO-GAC systems, bacteria colonize on the porous GAC surface where they are protected from high shear forces. Subsequently, biofilm remains active at very low target chemical concentrations, making the system less sensitive to toxic and inhibitory compounds and more resistant to loading shocks (Carvalho et al. 2001). BIO-GAC systems have been proven effective for removal of toluene (Irvine et al. 1992, Zhang et al. 2013).

However, this type of treatment has not been extensively studied under hypersaline conditions. Produced water is often characterized by high salinity, up to and over 400,000 mg/L as total dissolved solids (TDS) (Benko et al. 2008). High salt content inhibits biological treatment by causing plasmolysis and loss of cell activity in treatment systems, resulting in low organic removal efficiencies (Kargi et al. 1996). Furthermore, inorganic salts can slow BTEX adsorption if they precipitate and block access to the GAC surface (Randtke et al. 1983).

In this study, two lab-scale upflow anaerobic sludge bed (UASB) reactors were operated at the University of Kansas (KU) Environmental Microbiology Lab. A BIO-GAC reactor and a biological (BIO) reactor were fed with synthetic produced water with a composition based on

Sharghi et al. (2014), as shown in **Table 1**. The purpose of this study is to evaluate the removal of toluene from produced water by adsorption onto granular activated carbon with biofilm growth in a UASB system and analyze the effects of a hypersaline environment on removal efficiency.

***Table 1**: Synthetic produced water composition*

Compound	**Conc. (g/L)**
$CaCl_2 \cdot 2H_2O$	0.06
KCl	2
$MgCl_2 \cdot 6H_2O$	0.05
$NaHCO_3$	0.8
NH_4Cl	0.6
KH_2PO_4	0.099
Glucose	1.22
NaCl	0, 10, 20, 30
Trace Metals	0.2 mL/L

2.0 Literature Review

2.1 Produced Water Quality and Chemistry

In order to advance current treatment technologies for produced water and to determine appropriate reuse or disposal options, an understanding of produced water characteristics is necessary. Produced water components vary widely and largely depend on geographic location, geographic formation, and type of hydrocarbon product generated. The focus of environmental concern is on four major characteristics of produced water: salinity, organic compounds, inorganic compounds, and naturally occurring radioactive material (NORM) (Clark et al. 2009). Typical water quality of produced water is shown in **Table 2**.

***Table 2**: Typical Water Quality of Produced Water*

Parameter	Ranges in PW
TSS (mg/L)	1.2-1,000[1]
TDS (mg/L)	1,000-400,000[1]
COD (mg/L)	1,220[1]
NORM (pCi/L)	5-720[1]
pH	5.2-8.9[2]

[1](Guerra et al. 2011)

[2](Alley et al. 2011)

2.1.1 Constituents

Salinity is often expressed as total dissolved solids (TDS) and can be anywhere from 1,000 mg/L to over 400,000 mg/L (Benko et al. 2008). Produced water is typically more saline than seawater with the most abundant elements being sodium and chloride (Neff et al. 2011). The

difference in salinities can lead to major toxicity effects when produced water is discharged to surface water bodies.

Organic and inorganic content is dependent on the original chemical characteristics of the formation as well as chemical additives used to improve operations (Clark et al. 2009). In the majority of oil and gas produced waters, the most abundant organic chemicals are water-soluble low molecular weight organic acids and monocyclic aromatic hydrocarbons (Neff et al. 2011). Total organic carbon (TOC) is a constituent of concern that can range from less than 0.1 mg/L to over 11,000 mg/L in produced water (Neff et al. 2011). Monocyclic aromatic hydrocarbons such as benzene, toluene, ethyl-benzene and xylenes, commonly referred to as BTEX, are present in oil, partition into the produced water, and are one of the largest contributors to toxicity (Utvik 1999). Cations, anions, and heavy metals are also present in produced water and can cause problems with toxicity, scale formation, and salinity (Fakhru'l-Razi et al. 2009). NORM includes radionuclides such as uranium, thallium, radium, and radon. In produced water, NORM usually appears in the form of radium 226 and 228 (Veil et al. 2004). Radiation caused by these materials can severely damage the environment and threaten animal and human life.

It is especially important to investigate wells in Kansas as the state generates one of the largest volumes of produced water in the United States. Kansas is one of two states in the Western United States, along with Texas, with more than 25,000 oil wells and more than 25,000 gas wells (Guerra et al. 2011). Water produced in Kansas tends to have high salinity largely consisting of sodium chloride. Produced water in this region typically contains smaller amounts of the cations potassium, magnesium, and calcium. The radioactivity levels in Kansas basins are approximately five times greater than the median levels in the Western United States, indicating severe radioactivity and high concentrations of NORM (Guerra et al. 2011). These characteristics suggest

that produced water in Kansas needs a high level of treatment before it can be beneficially reused or disposed.

2.2 Produced Water Disposal

Produced water management by the petroleum industry is driven economically by the cost of the hydrocarbon present in the wastewater (Guerra et al. 2011). Throughout the history of the industry, disposal with minimal or no treatment has been the most common practice for oil and gas produced water management (Clark et al. 2009). Typical disposal methods are land and surface water discharge, discharge to publicly owned treatment works, and deep well injection.

2.2.1 Land and Surface Water Discharge

The cost of discharging produced water to land and surface water is low, but the practice has become increasingly rare in the United States. It is typically reserved only for high quality produced waters with relatively low risk of soil and water contamination (Guerra et al. 2011). In fact, direct discharge is prohibited east of the 98th meridian (Mueller 2015). The large exception to this is produced water resulting from offshore drilling, which is typically discharged to the ocean under a permit from the National Pollutant Discharge Elimination System (NPDES) operated by the United States Environmental Protection Agency (EPA) (Clark et al. 2009).

If land or surface water discharge is permitted for onshore wells, the EPA requires treatment dependent on the characteristics of the receiving soil or water body (Veil 2015). For example, produced water may be directly discharged to land or surface waters in Texas if it is west of the 98th meridian, and it meets stringent effluent requirements set forth by the EPA and the state regulatory agency, the Texas Railroad Commission (Humberson 2017). Furthermore, the treated

produced water must be beneficially reused for agricultural or wildlife use. Additional requirements are also necessary for discharge into impaired waters in the state.

It is important to note that in 2018, the EPA began a study focused on determining if changing federal regulations to allow for broader discharge of treated produced water to surface waters is justifiable (EPA 2019). The basis of the study is water scarcity in some arid regions of the United States. Augmenting surface water with large volumes of treated produced water would mitigate major drought issues in these areas. The EPA engaged with states, tribes, and stakeholders to gain individual perspectives and in a public meeting in October 2018, they reported their findings. Some states and tribes were supportive of allowing additional discharge for treated produced water with some concern regarding water quality impact, lack of contaminant knowledge, and required technical expertise. In addition, many industrial producers were supportive because of the additional flexibility new disposal practices would provide (EPA 2018). Considerations of these results should be taken as the EPA looks to possibly amend regulations in the future.

2.2.2 Discharge to Publicly Owned Treatment Works

Although direct discharge of pollutants into waters of the United States has been regulated and permitted since 1972 as a result of the Clean Water Act (CWA), indirect oil and gas produced water discharge via publicly owned treatment works (POTWs) went unenforced for years after (EPA 2016). Until recently, untreated or minimally treated produced water was commonly disposed of in this way.

Prior to 2016, discharge via POTWs was especially common in the state of Pennsylvania. Multiple studies highlighted the adverse effects caused by this disposal method. Hladik et al.

(2014) found elevated bromide levels and other organic disinfection byproduct (DBP) precursors at the outfalls of multiple Pennsylvania POTWs that accepted oil and gas produced water. Similarly, Warner et al. (2013) found that after a POTW received Marcellus Shale produced water, concentrations of chloride and bromide increased downstream above background levels, and radium levels in the sediments were ~200 times greater than upstream levels.

The results of these studies and others increased human and environmental health concerns related to produced water disposal. Moreover, pollutants in some produced waters caused disruptions in POTW wastewater treatment operations, causing even greater concern for human health and the environment (Ferrar et al. 2013). In response to these concerns, the EPA established pretreatment standards in 2016 for produced water discharged to a POTW, including a requirement for zero discharge of pollutants from the oil and gas industry to the POTW (EPA 2016). The new regulation effectively banned indirect discharge of oil and gas produced water to POTWs.

2.2.3 Deep Well Injection

Produced water disposal by deep well injection is currently practiced across the United States on a large scale (Burton et al. 2014), and for reasons of ease of operations and cost, this method is most used in the industry. In 2012, 93% of produced water from onshore wells was disposed of by injection (Veil 2015). The Safe Drinking Water Act (SDWA) of 1974 established the Underground Injection Control (UIC) program to regulate well injection. Regulation and operations of the UIC program occur at the state level under supervision by the EPA. The produced water is disposed of in Class II wells designated for fluids associated with oil and natural gas production (EPA 2018). As unconventional technologies such as horizontal drilling emerged, hydraulic fracturing expanded, resulting in a growing need for more Class II deep injection disposal wells with larger volumes of produced water (Bergman 2014).

In addition to disposal, Class II injection wells are used for what the industry calls enhanced recovery. This process is very common and involves re-injecting produced water into an oil or gas rich formation to aid in moving the desired product toward a production well for increased speed and volume of product (Thomas 2008). Of the 93% of onshore produced water injected underground in 2012, 46% of that was injected for enhanced recovery (Veil 2015).

A major concern regarding deep well injection is its effect on seismic activity in regions surrounding disposal wells (Bergman 2014). As produced water production and subsequent deep well injection increased rapidly in the 2000s, an increase in seismicity surrounding injection wells drew a direct correlation from the produced water industry. This is particularly true in the central US states of Kansas, Oklahoma, and Texas. This correlation between a significant increase in seismic activity, particularly in the central United States, and produced water reinjection volume illuminates the necessity for better management practices (Walsh et al. 2015). Kansas is the third largest state in terms of number of active produced water injection wells behind only Oklahoma and Texas (Weingarten et al. 2015). **Figure 1** shows the rapid increase in well count and produced water disposal volumes in two counties with the largest produced water injection in Kansas from 1985 to 2015 (KCC 2017). Prior to 2013, Kansas had less than two felt earthquakes in one year; however, that number has quickly increased since 2013. **Table 3** shows the number of felt earthquakes in Kansas each year from 2013 to 2018 (Buchanan 2015, KGS 2018). In response to the sharp incline in seismicity, the Kansas Corporation Commission (KCC) issued orders in March 2015 and August 2016 that limited hypersaline wastewater injection in five areas of concern in the state. Following these orders, the number of total earthquakes in the state was reduced by 66% (KCC 2017). It is imperative to find alternatives to deep well injection as orders such as these are put in place across the country.

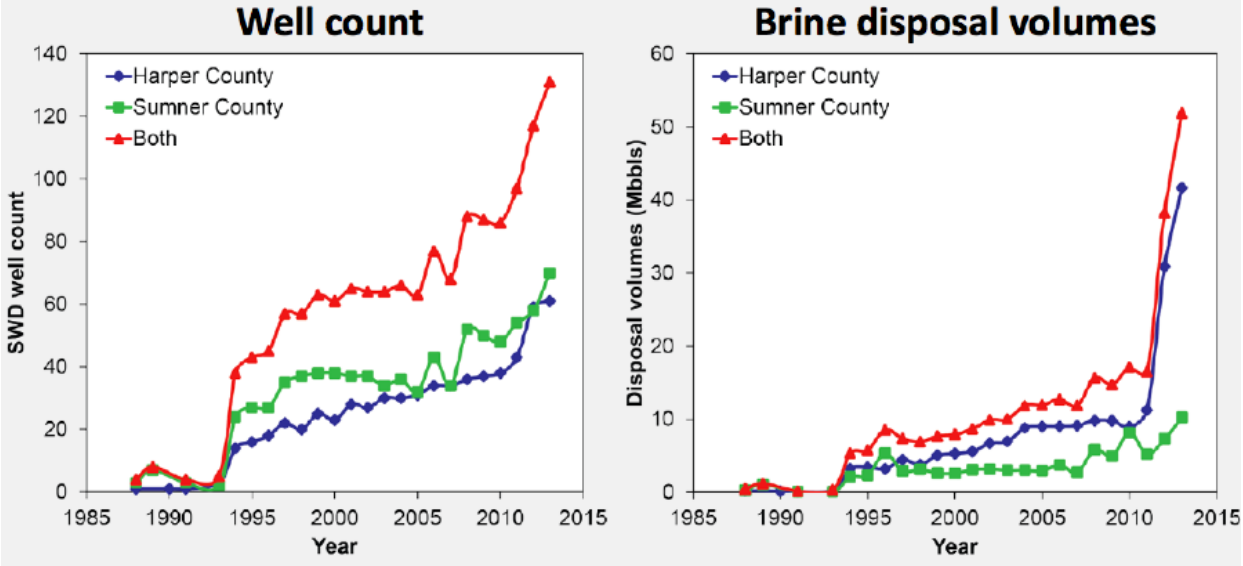

***Figure 1**: Well Count and Brine Disposal Volumes in Harper and Sumner Counties in Kansas in 1985-2015 (KCC 2017)*

***Table 3**: Felt Earthquakes in Kansas 2013-2018*

Year	Number of Felt Earthquakes (>2.5 magnitude)
2013	~10[1]
2014	< 100[1]
2015	132[2]
2016	159[2]
2017	208[2]
2018	127[2]

[1](Buchanan 2015)

[2](KGS 2018)

2.3 Produced Water Treatment Processes

Produced water is an abundant resource that if adequately treated can be used for other purposes including irrigation and agriculture that benefit public safety and economic prosperity. Irrigation in the Western United States accounts for over 70% of total state water usage (Kenny et al. 2009). Produced water can supplement the freshwater supply for irrigation if it is treated to meet water quality standards to avoid crop damage. Produced water can also be valuable for agricultural purposes including livestock feeding. Livestock feeding requires a relatively high level of water treatment, although not as high as for human drinking water. Reusing produced water in this way can be valuable in states where livestock farming is abundant and where the produced water production is also high (Clark et al. 2009, Kenny et al. 2009).

One of the most challenging aspects of produced water treatment is the integration of the technology into the oil and gas industries. As mentioned, deep well injection is the most common produced water management practice because of cost and availability as well as the additional benefit of enhanced recovery. In this way, some produced water is already beneficially reused. Some businesses such as Shell Oil Company have implemented additional programs focused on minimizing produced water volume, reducing costs associated with produced water treatment, and reusing produced water whenever they can (Khatib et al. 2003). An important step for research and development is to optimize treatment methods that are applicable for various companies across the country.

Beneficial reuse is dependent on the quality and removal efficiency of treatment processes. Water quality required for some examples of beneficial reuse is shown in **Table 4**. There are a number of treatment options currently available, but no single one of these processes is excellent at removing all constituents of concern from all produced waters. Therefore, the use of a hybrid

system involving a number of these methods will give the best results/best water quality (Guerra et al. 2011).

***Table 4**: Water Quality Required for Beneficial Reuse of Produced Water*

Parameter	Livestock Feeding	Irrigation	Enhanced Oil & Gas Recovery
TSS (mg/L)	< 30[2]	< 30[2]	N/A
TDS (mg/L)	< 10,000[1]	< 2,000[2]	<30,000[2]
BOD (mg/L)	< 30[2]	< 10[2]	N/A
NORM (pCi/L)	< 5[1]	< 5[1]	Low[2]
pH	6.0-9.0[2]	6.5-8.4[2]	N/A

[1](Guerra et al. 2011)

[2](Bastian et al. 2012)

[3](Alley et al. 2011)

2.3.1 Preliminary Treatment

Preliminary treatment of produced water often requires a number of steps and can often depend on treatment technologies that come after. Flow equalization can be used before a treatment process to account for the variability in produced water volume at a given time (Scanlon et al. 2014). In addition, neutralization may be necessary to adjust to appropriate pH levels for subsequent treatment (Theobald 2013). Other pretreatment steps that are utilized include, but are not limited to, screening, aeration, grit removal, chlorination, and oil and grease removal.

2.3.2 Coagulation and Flocculation

Coagulation and flocculation are basic conventional treatment processes that focus on suspended solids removal. Coagulation involves adding a chemical such as alum or ferric chloride

to the wastewater to neutralize the charge on suspended solids and oil droplets so they can be aggregated and then be settled or filtered out (Mazille et al. 2018). Flocculation complements coagulation by mechanically agitating the wastewater to encourage particle contact and create larger aggregates for better settling (Mazille et al. 2018). The technology is commonly used in municipal drinking water, wastewater treatment, or as a pretreatment step in industrial wastewater treatment including oil and gas produced water.

2.3.3 Chemical Precipitation

Chemical precipitation is similar to coagulation and flocculation in that it is utilized for solids removal. However, chemical precipitation aims to remove dissolved ions by the addition of counter-ions that create a reaction that results in solid particles that are then able to be settled or filtered out (Wang et al. 2005). Chemical precipitation has been commonly used for phosphorus removal in wastewater treatment (Morse et al. 1998). It is important to note that adding chemicals may result in unwanted or unforeseen byproducts when they react with oil and gas produced water. A complete understanding of the water's composition is essential to avoid these results.

2.3.4 Clarification

Physical separation is a basic treatment process that involves solid removal with or without addition of chemicals. Mechanisms such as gravity, electrical attraction, and physical barriers are used to treat the wastewater (Woodard 2001). Physical separation can be sedimentation, flotation, or filtration among others. Large tanks with low flow are typically used for sedimentation and flotation purposes. Filtration through conventional trickling rock filters, sand bed filters, or membranes is also commonly used. Technologies such as hydrocyclones also exist; this basically involves using the mobility of fluid flow in a mechanical unit to forcefully remove suspended

solids. Hydrocyclones are primarily used in produced water treatment to remove oil and sand (Changirwa et al. 1999).

2.3.5 Disinfection and Oxidation

Disinfection and oxidation are most often used toward the end of a full treatment process to sterilize or kill any bacteria that may remain in the treated effluent (Zimmermann et al. 2011). This is to prevent reproduction and subsequent water quality degradation later on. Disinfection-oxidation is most often achieved in wastewater treatment by chlorination, ozonation, or ultraviolet (UV) radiation. A major challenge associated with chlorination and ozonation is the possibility of forming disinfection byproducts which can adversely affect human and environmental health (Metcalf et al. 2007).

2.3.6 Membrane Processes

Treatment of wastewater by membranes has become increasingly more common in the last decade due to rapid advancements in membrane technology (Metcalf et al. 2007). Membranes are categorized into three types: pressure driven, electrically driven, and diffusion driven. Pressure driven membranes are the most common and include microfiltration (MF), nanofiltration (NF), ultrafiltration (UF), and reverse osmosis (RO). Electrodialysis (ED) is an electrically driven membrane system whereas dialysis and forward osmosis (FO) are diffusion driven. Membranes are generally used for dissolved contaminant removal which provides benefits to produced water treatment. For example, Walker et al. (2014) successfully removed 99% salinity from a brackish wastewater using a RO-ED system. In addition, Abadi et al. (2011) were able to achieve 95% TOC removal and 4 mg/L O&G effluent concentration by treating oilfield produced water with a tubular ceramic MF system.

Membrane bioreactors (MBRs) that combine membrane technology with biological treatment are becoming increasingly popular in the wastewater industry due to their ability to remove a wide range of contaminants (Judd 2010). However, these technologies have some disadvantages that prevent them from being implemented at full-scale in many treatment operations. MBRs have higher capital and operation and maintenance (O&M) costs than conventional activated sludge (CAS) and MBRs often have significant fouling issues (Xiao et al. 2019) (Mondal et al. 2008). In addition, membranes are known to have a relatively short lifespan (5-10 years) compared to conventional treatment technologies (Metcalf et al. 2007). Nonetheless, some full-scale MBR systems have been implemented in treatment facilities in the United States and particularly in Europe, and research has shown that MBRs can be beneficial for produced water treatment (Melin et al. 2006, Pendashteh et al. 2012, Sharghi et al. 2014)

2.3.7 Thermal Distillation

As discussed, one of the most prominent and challenging contaminants in produced water is salinity. A desalination technique called thermal distillation is a potential solution and is available in three forms. Multiple-stage flash distillation is the most common and involves vaporization of the hypersaline wastewater at low temperatures in a vacuum (Khan 1986). Multiple-effect distillation similarly uses heating for evaporation but consists of multiple stages in which heat by steam is applied to the wastewater at which point some of the wastewater evaporates and then contributes to the steam heat for the next stage (Mistry et al. 2013). Vapor compression distillation uses increased pressure and temperature to create condensed steam to heat and evaporate hypersaline wastewater (Aly et al. 2003). All of these systems can be utilized for produced water treatment, however, because the wastewater is evaporated, it is unable to be beneficially reused without condensing the steam back to liquid form.

2.3.8 Adsorption and Ion Exchange

Physical adsorption is commonly used for treatment of produced water. Granular activated carbon (GAC) and powdered activated carbon (PAC) are most often the media used for adsorption of organic contaminants (Kristiana et al. 2011, Campo et al. 2017). Physical adsorption by activated carbon can also be combined with electrical treatment for desalination purposes of hypersaline wastewater (Chang et al. 2011).

A more common approach to desalination is ion exchange (Benko et al. 2008). The technology requires a resin loaded with charged ions that are exchanged with ions in the wastewater for removal from the liquid. Natural resins are available for ion exchange as are synthetic resins made with specifications in mind for specific treatment purposes (Rieman et al. 2013). Radon and boron are also able to be removed from wastewater using ion exchange technology (Stein 1985, de la Fuente et al. 2005). Ion exchange, however, is most often used for low TDS waters and not very common for hypersaline produced water. Additionally, one of the major hindrances of utilizing adsorption or ion exchange technology is the high cost often associated with media and resin type (LeVan et al. 1997, Dias et al. 2007). Careful cost considerations must be made when determining the best treatment systems for produced water.

2.3.9 Evaporation Ponds

Evaporation ponds for produced water treatment are limited by location and are usually found only in arid or semi-arid climates with an abundance of solar energy (Ahmed et al. 2000). The basic principle of evaporation ponds is filling a shallow pit with hypersaline water and waiting for the water to evaporate.

A major concern associated with evaporation ponds is the high concentration of solids left over after liquid evaporation (Ahmed et al. 2000). Kavvadias et al. (2010) showed that the underlying soil of evaporation ponds used for oil mill waste disposal had significantly increased contaminant levels 6 years after the practice ended, concluding that there was risk for groundwater contamination. In response to this concern, most regulation now requires pits to be lined for produced water storage or evaporation to protect underlying soil and aquifers (Lenntech 2019).

2.3.10 Zero Liquid Discharge

In addition to evaporation ponds, other zero liquid discharge (ZLD) technologies include mechanical spray evaporation, brine concentration, and crystallization. Zero liquid discharge uses thermal evaporation to produce a high quality liquid effluent and solids that can both be reused (Charisiadis 2018). Unlike evaporation ponds which require large land area, these systems are relatively compact. Similarly to evaporation ponds, these technologies are generally limited to arid or semi-arid regions.

2.4 Toluene

As mentioned previously, BTEX compounds are commonly found in produced water across the United States. Toluene, being a member of the BTEX group, is found in produced water from conventional oil and gas wells, ranging from non-detect (ND) to 37 mg/L with a median concentration of 9.7 mg/L (Fillo et al. 1992). Toluene is a focal point in recent research aimed at removing harmful BTEX contaminants from produced water as federal regulations require low levels for aquatic and human safety. The EPA specifies a chronic ambient water quality criterion

(AWQC) and a domestic water supply maximum contaminant level (MCL) for toluene of 1000 µg/L (EPA 2000).

2.4.1 Chemical Stability

Toluene is an aromatic hydrocarbon; it has a basic ring-like structure shown in **Figure 2**. The ring makes it very stable and incredibly difficult to break down for treatment purposes (England et al. 1971).

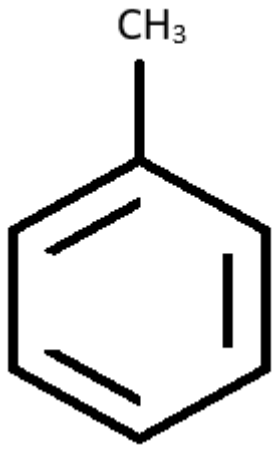

***Figure 2**: Toluene Chemical Structure*

2.4.2 Volatility

Toluene is extremely volatile at room temperature and has a low solubility in water. Therefore, some vaporization of toluene from wastewater is common and should be expected; this poses a significant risk to human health (WHO 2000). In addition, there is a heightened risk when working with toluene in research in a laboratory setting; precautions should be taken to minimize loss of toluene through vaporization.

2.4.3 Toxicity

Although benzene is a known carcinogen, there is inadequate information to suggest toluene is a carcinogen (EPA 2016). However, toluene is toxic to humans at concentrations as low as 5 µg/L (EPA 2016). Acute exposure can lead to symptoms including but not limited to headache, dizziness, confusion, nausea, blurred vision, vomiting, diarrhea, and irritation to the skin, eyes, and respiratory tract. Extreme symptoms of acute toluene exposure can be hallucinations, tremors, seizures, and coma. Chronic exposure can cause headache, fatigue, and nausea in addition to coordination and memory loss, permanent muscular and cardiovascular disorders, and death (CDC 2014).

2.5 Granular Activated Carbon

GAC is known to be a high-performing adsorbent because of its high surface area and porous structure, which gives it a high adsorption capacity (Dias et al. 2007). It has been used for years for industrial wastewater treatment purposes.

2.5.1 Treatment of Organics by Adsorption

GAC has been shown in numerous studies to effectively remove organic compounds from water, and many types are readily available in the industry (Randtke et al. 1983, Scott et al. 1995, Paune et al. 1998). Other studies have been done that provide evidence for GAC's ability to remove organic micropollutants such as BTEX compounds (including toluene) from produced water (Gallup et al. 1996, Seybold et al. 1997, Doyle et al. 2000). A summary of three studies' BTEX removal efficiencies is shown in **Table 5**. The most common treatment for toluene removal from wastewater is activated carbon adsorption (Wibowo et al. 2007).

***Table 5**: BTEX removal results of studies utilizing GAC adsorption*

Study	BTEX Removal
Gallup et al. 1996	98%
Seybold et al. 1997	99.9%
Doyle et al. 2000	99.8%

2.5.2 Types

Types of GAC promoting different surface areas, pore sizes, etc. are widely available on the market. A comparison of GAC types is often necessary to determine the best type for a specific treatment purpose, in this case, toluene adsorption. Randtke et al. (1983) identify key parameters that can affect adsorptive capacity including carbon preparation, GAC dosages, and adsorbate concentration among others. It is important to take these into consideration when determining the type of GAC to use in an adsorption system.

2.6 Biological Treatment

Current treatment technologies practiced by the petroleum industry are focused on removal of heavy metals, O&G, suspended solids, and salinity expressed as TDS (Igunnu et al. 2012). For removal of organics from produced water, it is well known that biological treatment is effective. Woolard et al. (1995) showed that biological treatment for removal of organics from hypersaline wastewater was possible by selecting for halophilic organisms; a halophilic sludge sequencing batch reactor (SBR) operated at 15% (150 g/L) salinity had an average phenol removal of over

99.5%. Similarly, Sharghi et al. (2014) studied utilizing halophilic organisms in a membrane bioreactor for high salinity produced water and achieved 81.6-94.6% chemical oxygen demand (COD) removal.

A major area of concern with current biological treatment is the limited processes for the removal of trace organic micropollutants, specifically aromatic hydrocarbons including toluene. Because biological treatment is quite common in the industry, there are efforts to improve biological treatment of toluene. Although biodegradation of toluene is possible, research shows that biodegradation is limited by the rate of desorption from cells (Zhang et al. 1997). However, recent advancements in research including combining biological and physical treatment have provided promising results in moving toward more effective, cost efficient methods to treat produced water for trace organics. A BIO-GAC hybrid system which utilizes biofilm growth on granular activated carbon can provide advantages for simultaneous removal of BTEX and other produced water contaminants.

2.6.1 Biofilm on Granular Activated Carbon

As mentioned, GAC has been proven to be effective at removing organics including toluene by adsorption due to its highly porous structure and graphite surface chemistry (Wibowo et al. 2007). The structure of GAC including its high surface area and roughness also make it a good candidate for biofilm attachment. Moreover, studies show that natural biological growth is common on GAC treatment systems where the GAC is not regularly replaced or regenerated (Lee et al. 1981, Servais et al. 1991, Moll et al. 1999, Velten et al. 2007, Hammes et al. 2008).

Irvine et al. (1992) tested an aerobic BIO-GAC reactor for BTEX removal and obtained >99.9% toluene removal. Similarly, Zhang et al. (2013) achieved almost complete toluene removal

from wastewater utilizing BIO-GAC columns. Utilizing GAC and biology in this way can provide effective toluene removal while providing the same or better treatment results for produced water as conventional biological treatment. Xing et al. (2008) completed a side-by-side comparison of GAC adsorption and GAC biosorption on dissolved organic carbon (DOC) removal and found that GAC biosorption performed significantly better than GAC adsorption in all of their tests.

2.7 Broader Impacts

Most research utilizing BIO-GAC treatment for toluene removal is conducted under aerobic conditions. Because toluene and other BTEX chemicals are volatile compounds, aerobic systems increase the risk of vaporization which can lead to poor air quality and adverse health effects. In addition, most studies to date are conducted on wastewater with little or no salinity. Few studies are available on the efficiency of toluene removal from hypersaline wastewater utilizing BIO-GAC operated under anaerobic conditions. Studies show that halophilic bacteria are able to metabolize aromatic hydrocarbons including toluene (Le Borgne et al. 2008, Sei et al. 2009). This indicates that selecting for halophilic bacteria in a BIO-GAC system is effective for toluene removal from produced water. Making progress toward optimizing such a system that incorporates the use of BIO-GAC to effectively treat oil and gas produced water for the removal of toluene under anaerobic hypersaline conditions is the focus of this research.

3.0 Methods and Procedures

3.1 Reactor Setup

Two 3.7-L upflow anaerobic sludge bed (UASB) reactors, see **Figure 3**, were operated at the KU Environmental Microbiology Lab. The internal diameter of each reactor was 6.4 cm and each had a height of 96 cm. Seed granular sludge for the reactors was anaerobic granular sludge from a UASB reactor used to pre-treat select industrial wastewater streams at the City of Cedar Rapids, IA Water Pollution Control Facility. One experimental BIO-GAC reactor was loaded with Filtrasorb 400 GAC (Calgon Carbon Co., Pittsburgh, PA) added at 35% reactor volume, in addition to seed granular sludge, and one control BIO reactor was loaded with granular sludge only. Sludge was added to obtain a mixed liquor volatile suspended solids (MLVSS) of 6,000 mg/L in both reactors. GAC was washed and filtered through a 300 µm sieve until water ran clear to limit the effects of smaller particles and dust, which would contribute to effluent suspended solids if dislodged in an upflow reactor.

The reactors were operated with continuous flow at a target hydraulic residence time (HRT) of 10 hours. Pumping the wastewater in and out of the reactors was performed with peristaltic pumps (Cole-Primer model 7524). A Masterflex® L/S model no. 07528-10 variable-speed peristaltic pump was used to recycle flow within the reactors and achieve an upflow velocity of 1.25 m/h. No sludge bed fluidization was observed at this low recirculation rate. A Fisher Scientific® Isotemp circulating water bath was utilized to keep the temperature of both reactors at 35°C throughout experimentation. In phase I the reactors were operated consistently for 150 days before the start of toluene addition and experimentation. Phase II then began when toluene was added to both reactors at 10 mg/L based on the median concentration found in produced water from conventional oil and gas wells (Fillo et al. 1992). After 60 days of phase II, phase III

commenced when salinity was added to both reactors to determine its effects on reactor performance.

***Figure 3**: Photo of UASB reactors at the KU Environmental Microbiology Lab*

3.2 Synthetic Produced Water Composition

The reactors were fed synthetic produced water with a composition based on Sharghi et al. (2014), as shown in **Table 6**. Compounds added in the trace metal solution are listed in **Table 7**. Target COD of the synthetic produced water was 1300 mg/L based on typical ranges in real

produced water (Guerra et al. 2011). Glucose remained the only carbon source throughout operation until toluene addition. The reactors were bottom fed to establish plug flow conditions. In phase III of experimentation, salinity was added to the influent of both reactors by adding NaCl. Salinity was increased incrementally by 1% (10 g/L) on a weekly basis starting at 1% and ending at 3%. During phase III, the toluene feeding target remained at 10 mg/L in the influent.

***Table 6**: Synthetic produced water composition*

Compound	**Conc. (g/L)**
$CaCl_2 \cdot 2H_2O$	0.06
KCl	2
$MgCl_2 \cdot 6H_2O$	0.05
$NaHCO_3$	0.8
NH_4Cl	0.6
KH_2PO_4	0.099
Glucose	1.22
NaCl	0, 10, 20, 30
Trace Metals	0.2 mL/L

***Table 7**: Trace metals composition*

Compound	**Conc. (g/L)**
FeCl3*6H2O	1.5
H3BO3	0.15
CuSO4*5H2O	0.03
KI	0.03
MnCl2*4H2O	0.12
Na2MoO4*2H2O	0.06
ZnSO4*7H2O	0.12
CoCl2*6H2O	0.15

3.3 Biofilm Attachment

The experimental BIO-GAC reactor was seeded with Cedar Rapids, IA UASB granules to encourage biofilm growth on the GAC particles. This mesophilic granular methanogenic sludge was chosen because of its ability to treat high-strength industrial wastewater in a UASB reactor similar to the lab-scale UASB reactors at KU. Before inoculating, sludge was sieved through a 200 µm sieve to ensure only granules >0.2 mm were used. The settling velocity of the UASB granules was measured at 75 m/h. As mentioned above, sludge was added to obtain a MLVSS of 6,000 mg/L in both reactors.

3.3.1 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was utilized to confirm biofilm attachment on the GAC particles in the experimental reactor. In this methodology, a beam of electrons scans the surface of a sample to obtain imaging of surface topography and composition (Castle et al. 1997). An FEI VERSA 3D Dual Beam instrument at the KU Microscopy & Analytical Imaging Lab (MAI), shown in **Figure 4**, was used to scan individual GAC particles from the reactor.

***Figure 4**: FEI VERSA 3D Dual Beam instrument used for SEM imaging*

3.3.1.1 Sample Preparation

GAC samples taken from the BIO-GAC reactor were fixed with paraformaldehyde for 4 h at 4°C. The samples were then washed with increasingly concentrated ethanol solutions (30%, 50%, 70%, 90%, and 100%) for 10 minutes each according to Bassin et al. (2012). Individual GAC particles were then placed around the edges of a turntable for SEM imaging. A fresh, unused GAC particle was also imaged as a control. Some buildup of electrons on the particle surface causing image distortion, known as charging, occurred in the samples. Coating the particle surface with a thin film of gold is a common way to avoid charging and should be practiced in future work (Leslie et al. 2007).

3.4 DNA Quantification

Before biofilm attachment on GAC was confirmed, deoxyribonucleic acid (DNA) samples from both reactors were taken and quantified to ensure bacteria were growing as necessary in the system. Samples were prepped by centrifuging mixed liquor at 10,000 g for 3 minutes after which the supernatant was pipetted out leaving behind a pellet. Samples were stored at -20°C until DNA extraction.

3.4.1 PowerBead DNA Extraction

DNA was extracted from the samples using a QIAGEN DNeasy PowerSoil Kit, following instructions from the company protocol accompanying the kit.

3.4.2 Qubit High Sensitivity Analysis

Once extracted, DNA was quantified using a Qubit dsDNA HS Assay Kit with a Qubit 2.0 Fluorometer, shown in **Figure 5**. Instructions were followed from the company protocol accompanying the kit.

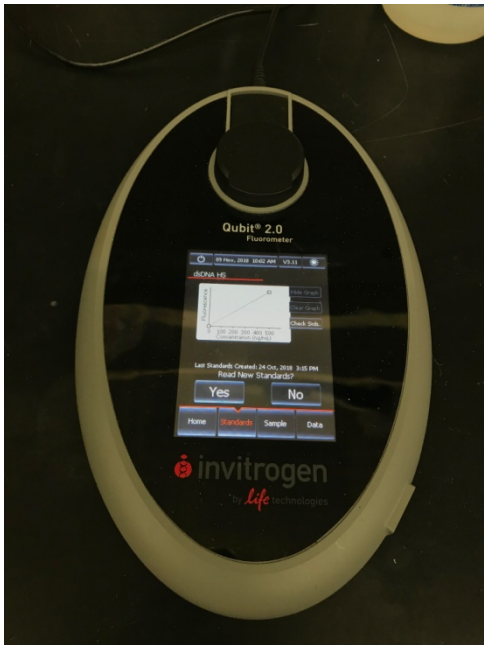

***Figure 5**: Photo of Qubit 2.0 Fluorometer used in the experiment*

3.5 Chemical and Solids Analyses

Chemical and solids analyses were conducted on samples from the reactors throughout the experiment to quantify carbon removal of COD and toluene and to monitor solids wasting in the system.

3.5.1 Chemical Oxygen Demand

COD was used as a measurement of carbon removal within both reactors. Hach high range digestion solution vials for 20-1500 mg/L COD were filled with 2 mL of sample, mixed, digested using a Hach DRB 200 digester at 150°C for 2 hours, cooled to room temperature, and read by a Hach DR 5000 UV spectrometer. A vial with 2 mL of Milli-Q water was used as a blank to zero the instrument.

3.5.2 Suspended Solids

Measurement of total effluent suspended solids (ESS) was performed according to ASTM Standard D5907-18. Additionally, effluent volatile suspended solids (EVSS) was measured after ESS by heating the filters in a furnace to 550°C for 20 minutes and then weighing them. The difference in ESS final weight and EVSS final weight divided by the sample volume is the concentration of EVSS in mg/L.

3.5.3 pH

A pH range of 7.2-7.5 was targeted for the influent synthetic produced water to maintain neutral pH within the system. Hydrochloric acid was added when making the synthetic produced water to control influent pH.

3.5.4 Toluene Measurements

Because of its high volatility at room temperature, toluene is difficult to quantify without a well-developed method.

3.5.4.1 Solid Phase Micro-Extraction

Solid phase micro-extraction (SPME) is a sampling technique that involves the use of a fiber coated with an extracting phase, in this case a polymer, Carboxen®/polydimethylsiloxane

(CAR/PDMS). The SPME fiber is attached to a syringe which allows the fiber to move into and out of a protective needle. Organics are adsorbed onto the polymer fiber coating when the fiber is exposed to the sample. **Figure 6** shows the SPME syringe and needle with the fiber unexposed. The SPME fiber and holder used were manufactured by Supelco®, Cat no. 57318 and 57330-U, respectively.

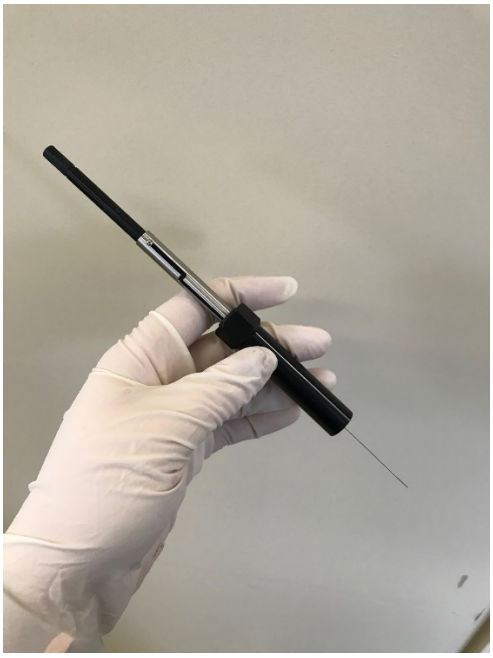

***Figure 6**: Photo of syringe and needle encasing SPME fiber*

Headspace sampling is a preferred method to extract volatile organic compounds such as toluene and was used in this experiment. Samples were collected and filtered through 0.45 µm glass fiber filters before SPME analysis in 20 mL glass vials with plastic caps lined with silicone septa. The vials were filled with 11 mL of sample before adding 1 ± 0.05 g NaCl to aid in toluene volatilization. Once capped, the vial was shaken until complete dissolution of NaCl and the vial

was then placed in a 50°C water bath and allowed to acclimate for 5 minutes. Mixing was continued in the water bath at 350 rpm. The syringe was then placed above the vial and the needle was passed through the vial septum. The SPME fiber was then exposed in the headspace just above the stirring vortex of the sample and left for 24 minutes of adsorption. Once the adsorption step was complete, the SPME fiber was retracted into the needle which was removed from the vial septum. The syringe was then transferred to the gas chromatograph for manual injection. The setup for this process is shown in **Figure 7**.

***Figure** 7: Photos of SPME sample adsorption process*

3.5.4.2 Gas Chromatography

Gas chromatography (GC) was the method used for quantification following extraction with SPME. It involves injecting the adsorbed sample onto the head of a chromatographic column through which the organics are transported by the flow of an inert, gaseous mobile phase, in this

case hydrogen gas. The GC is coupled with a mass spectrometer (MS) that allows the separation, identification, and quantification of chemicals. The result is a chromatogram with peaks that represent different chemicals and their respective quantities. An example of such a chromatogram is shown in **Figure 8**.

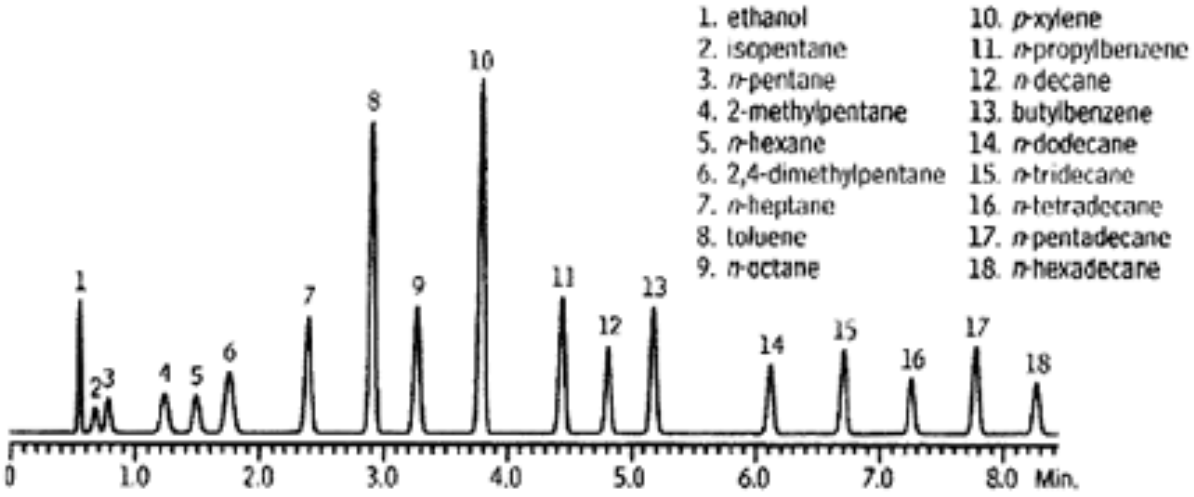

***Figure 8**: Chromatogram of Simulated Distillation Reference Mix (Froehlich 2007)*

An Agilent 7890B GC equipped with an Agilent 5977A mass selective detector, shown in **Figure 9**, was used in this experiment. The GC was equipped with an Agilent 19091S-433UI HP-5ms Ultra Inert GC capillary column and a Supelco® SPME injection sleeve (0.75 mm ID), Cat No. 26375. Once the toluene was extracted onto the polymer-coated fiber by SPME, it was manually injected into the GC by inserting the syringe into the heated GC injection port, passing the needle through the septum, and exposing the fiber for 5 minutes before retracting the fiber and lifting the syringe from the GC port. The sample run time was approximately 30 minutes.

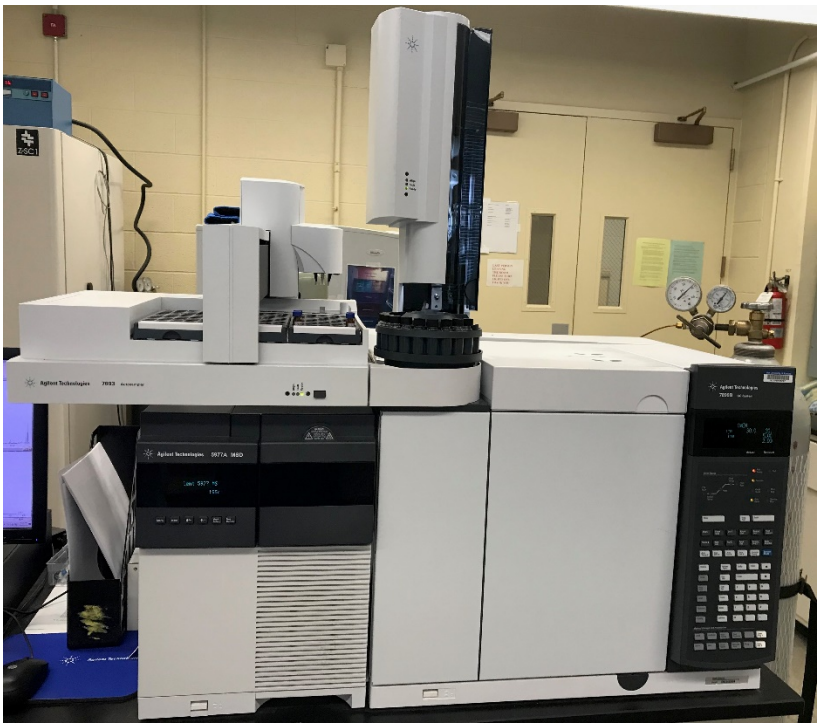

***Figure 9**: Agilent 7890B Gas Chromatograph with Agilent 5977A mass selective detector*

Two main methods were used on the GC, a Selected Ion Monitoring (SIM) method and a scan method. SIM is used to target specific compounds in a sample. In this experiment, a SIM method was used to target toluene on samples when only the toluene concentration was desired. A scan method provides a comprehensive chromatogram including all compounds identified by the GC. A scan method was used in this experiment to quantify all volatile substances adsorbed to the SPME fiber in addition to toluene. Details on the program specifics for the SIM and scan methods are provided in Appendices A and B, respectively.

3.6 Safety

Due to toluene's high level of toxicity and volatility, working with it in the lab requires important safety precautions.

3.6.1 Toluene Storage and Handling

The major focus of the safety plan was to prevent vaporization of toluene to the air outside and surrounding the reactors and related equipment. To achieve this, all equipment including both reactors, influent and effluent tanks, pump heads, and tubing were completely sealed. To prevent pressure buildup, pressure relief was provided in both reactors and in the influent and effluent tanks through tubing which led air to a snorkel in the lab, shown in **Figure 10**. As a precaution in case of excess toluene in the liquid stream after flow through the reactors, two additional GAC columns, shown in **Figure 11**, were utilized to further adsorb toluene before discharge to the effluent storage tank. The internal diameter of the columns was 5 cm and each had a height of 21 cm. The same Filtrasorb 400 GAC manufactured by Calgon Carbon Co. was used in these columns as in the BIO-GAC reactor. On the top and bottom of the columns, 2.5 cm was filled with glass wool to keep the GAC in place. The columns were also sealed to prevent vaporization of residual toluene to the surrounding air.

***Figure 10**: Photo of snorkel used for toluene ventilation*

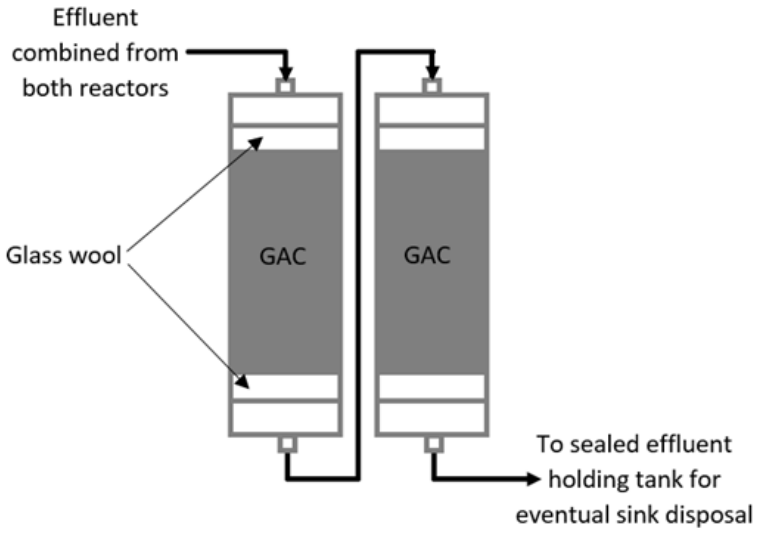

***Figure 11**: Schematic of effluent GAC columns*

To prevent vaporization when making the synthetic produced water, a separate tank was used to mix all chemicals in water except for toluene. This water was then pumped into the sealed influent storage tank that fed the reactors. Toluene was added separately by first mixing a stock solution in a laboratory fumehood and then using a syringe and butterfly valve to inject the stock solution into the sealed influent storage tank. At the end of the process, to dispose of effluent liquid waste, a peristaltic pump was connected to the sealed effluent tank. The water was subsequently pumped to a nearby sink for disposal.

Sampling was also performed in such a way to avoid vaporization of toluene. A three-way ball valve was connected to the effluent ports of each reactor such that flow that normally went to the GAC columns could be diverted to separate tubing. A female quick-connect fitting was attached to the end of each tube to keep the system closed. Two 50 mL vial caps were drilled, and the male quick-connect fittings were glued to the tops of these caps. To obtain a sample, the valve was opened to the additional tubing and a 50 mL vial with the quick-connect cap was connected

to the quick-connect tubing. Effluent was then able to flow into the vial. A similar process was used for sampling the influent, in which a quick-connect fitting was permanently attached to the influent tubing just after the influent pump. This quick connect was unattached and the female quick-connect was connected to a 50 mL vial with a male quick-connect cap for sampling.

The KU Department of Environment, Health & Safety (EHS) was consulted throughout the experiment on the planning, implementation, and monitoring of the sealed system. They approved all operations related to this safety plan.

3.7 Development of a Standard Curve for Toluene

To quantify toluene using SPME and GC analysis, development of a standard curve based on known toluene concentrations was necessary. Both high and low concentrations standard curves were developed to provide templates for a wide range of sample results. The standards were known quantities of toluene mixed in Milli-Q water, sealed with no headspace, and stored at 4°C when not in use. The standards were then run through the SPME and GC analysis outlined in Section 3.6 Toluene Measurements. **Figure 12** and **Figure 13** show the results graphically for the high and low standard curves, respectively. The regression lines indicate good correlation for both curves as the R^2 values are above 0.98 (Nau 2018). Because of the GC's upper limit of toluene measurement (around 1000 µg/L), samples were diluted before SPME in order to be measurable by GC. These standard curves were used to quantify results from the GAC comparison study and isotherm tests.

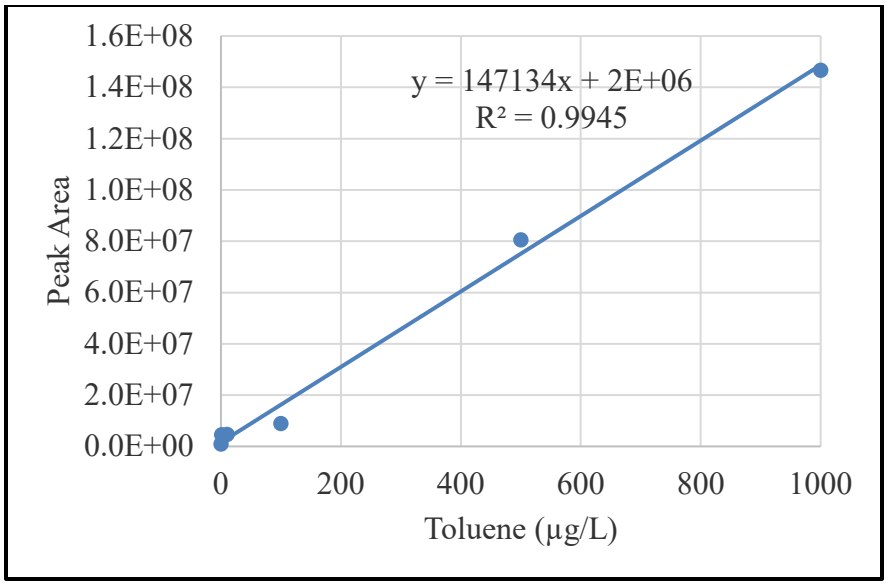

***Figure 12**: High value toluene standard curve*

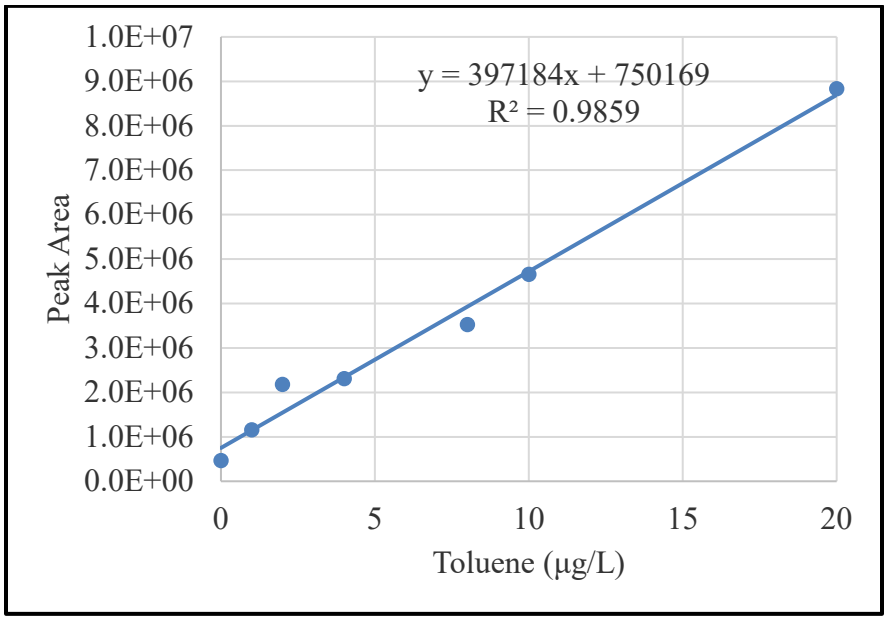

***Figure 13**: Low value toluene standard curve*

Before toluene in experimental reactor samples was quantified, a third standard curve was created to account for the synthetic produced water matrix. To do this, known quantities of toluene were mixed with the pre-mixed synthetic produced water described in Section 3.2 Synthetic Produced Water Composition. **Figure 14** graphs the standard curve results. The regression line

indicates good correlation with an R^2 value of 0.98 (Nau 2018). This standard curve was used to quantify all reactor influent and effluent samples during experimentation.

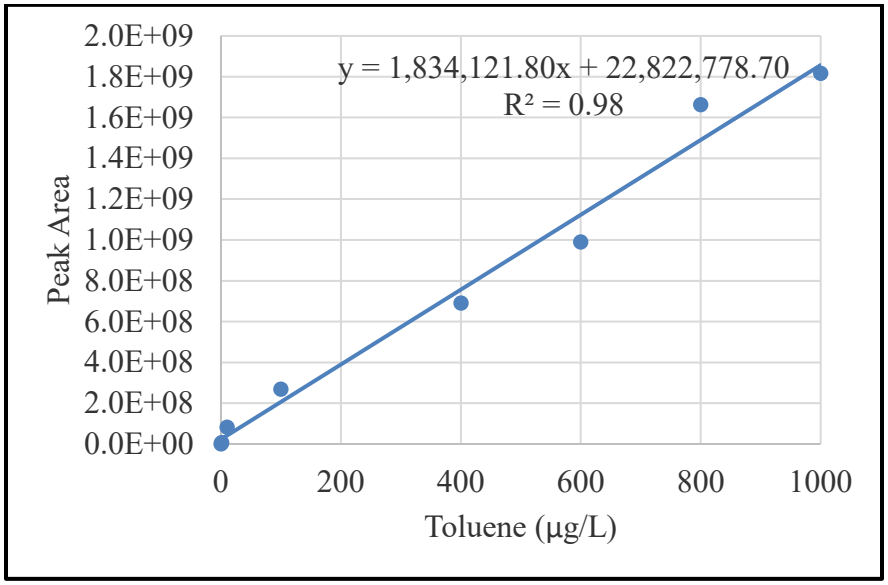

***Figure 14**: Toluene and synthetic produced water matrix standard curve*

3.8 Determination of Method Detection Limit

A method detection limit (MDL) for SPME and GC analysis was determined based on the following equation (EPA 2016):

$$MDL_S = t_{(n-1,1-\alpha=0.99)} S_S$$

where:

MDL_S = the method detection limit (µg/L)

$t_{(n-1,1-\alpha=0.99)}$ = the Student's t-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom (unitless)

S_S = sample standard deviation of the replicate sample analyses (µg/L)

Six replicates of 1 µg/L toluene in Milli-Q water were analyzed. **Table 8** lists their estimated toluene concentrations based on the low value toluene standard curve.

***Table 8**: MDL replicate sample results*

Replicate	Toluene (µg/L)
1	1.44
2	1.15
3	1.25
4	1.59
5	1.17
6	0.81

These results give a standard deviation of 0.268 µg/L. Using a $t_{(5,1-\alpha=0.99)}$ value of 3.365 for 6 replicates with 5 degrees of freedom at 99% confidence (Loch 2015), the MDL can be calculated:

$$MDL_S = 3.365 * \frac{0.268\mu g}{L}$$

$$MDL_S = 0.90\ \mu g/L$$

Based on this detection limit, any toluene concentration below 0.90 µg/L in an experimental sample was recorded as a non-detect (ND).

4.0 Results and Discussion

4.1 Comparison of Granular Activated Carbon Types

Prior to startup of the laboratory-scale reactors, a comparison test of five types of GAC obtained from two manufacturers was conducted to determine the GAC type used for the remainder of the experiment. **Table 9** lists the GAC types along with their respective manufacturers. These were chosen based on common use in the industry and availability.

***Table 9**: GAC types and manufacturers*

GAC	Source
DSR-C	Calgon Carbon Co., Pittsburgh, PA
Filtrasorb 200	Calgon Carbon Co., Pittsburgh, PA
Filtrasorb 400	Calgon Carbon Co., Pittsburgh, PA
Hydrodarco 820	Cabot Corporation
Hydrodarco 3000	Cabot Corporation

To test the adsorptive capacity of each GAC type, a 24-hour test was conducted. Glass serum bottles sized at 200 mL were rinsed with methanol, acid washed, and rinsed again with Milli-Q water several times before being filled with 1000 mg of GAC, filled to the rim with pre-mixed 10 mg/L toluene in Milli-Q water, and sealed with no headspace. The serum bottles were then put on their sides on a shaker table in an incubator set at 30°C at 250 rpm. After 24 hours, the bottles were uncapped, and supernatant was taken from the top and filtered through 0.45 µm glass-fiber filters before running SPME and GC analysis. The samples were run in duplicates to ensure precision. Two controls with no GAC were also tested to account for natural losses in the experiment.

Table 10 shows the average toluene removal efficiencies for the controls and each of the GAC types determined by SPME and GC analysis. Around 35% of toluene was lost from the controls with no GAC indicating significant loss due to vaporization, sorption to the glassware, or analytical losses. However, removal efficiencies calculated using the control value as the influent value still gave removal efficiencies greater than 98.5% for each GAC type indicating good toluene adsorption across the board. The best performances above 99% removal were obtained using Filtrasorb 200 and Filtrasorb 400 (Calgon Carbon Co.) at 99.2% and 99.1%, respectively.

***Table 10**: GAC toluene adsorptive capacity comparison results*

GAC	Removal	Removal relative to control
Control (no GAC)	35.1±0.2%	0.0±0.3%
DSR-C	99.1±0.1%	98.7±0.2%
Filtrasorb 200	99.5±0.0%	99.2±0.0%
Filtrasorb 400	99.4±0.1%	99.1±0.1%
Hydrodarco 820	99.1±0.2%	98.6±0.4%
Hydrodarco 3000	99.3±0.6%	98.9±1.0%

Both Filtrasorb 200 and Filtrasorb 400 removed over 99% of toluene in the comparison test. Specifications for these two GAC types provided by Calgon Carbon Co. are shown in **Table 11** and **Table 12**, respectively. Filtrasorb 400 was finally selected for its larger iodine number. Iodine number is a measurement of the milligrams of iodine adsorbed by one gram of carbon and is a common parameter used to indicate GAC surface area and characterize performance (ASTM 2014). Filtrasorb 400 has been shown to have high adsorptive capacity for toluene, so its high performance was expected. Tests by Canzano et al. (2014) resulted in an average adsorptive capacity of 327 mg toluene/g Filtrasorb 400. Simpson et al. (1993) demonstrated an even higher adsorptive capacity of 553 mg toluene/g Filtrasorb 400.

***Table 11**: Filtrasorb 200 specifications (Calgon Carbon Co. 2018)*

Specifications	
Iodine Number (mg/g)	850 (min)
Moisture by Weight (%)	2% (max)
Effective Size (mm)	0.55-0.75
Uniformity Coefficient	1.9 (max)
Abrasion Number	75 (min)
Screen Size by Weight, US Sieve Series	
On 12 mesh (%)	5% (max)
Through 40 mesh (%)	4% (max)
Typical Properties	
Apparent Density (tamped) (g/cc)	0.58
Water Extractables (%)	<1%
Non-Wettable (%)	<1%

***Table 12**: Filtrasorb 400 specifications (Calgon Carbon Co. 2018)*

Specifications	
Iodine Number (mg/g)	1000 (min)
Moisture by Weight (%)	2% (max)
Effective Size (mm)	0.55-0.75
Uniformity Coefficient	1.9 (max)
Abrasion Number	75 (min)
Screen Size by Weight, US Sieve Series	
On 12 mesh (%)	5% (max)
Through 40 mesh (%)	4% (max)
Typical Properties	
Apparent Density (tamped) (g/cc)	0.54
Water Extractables (%)	<1%
Non-Wettable (%)	<1%

4.2 Adsorptive Capacity of Filtrasorb 400 Granular Activated Carbon

Before reactor startup, determining the adsorptive capacity of Filtrasorb 400 for toluene was necessary.

4.2.1 Sorption Isotherm

A sorption isotherm is often used in adsorption to characterize the ability of GAC to remove a particular contaminant from water (EPA 2019). It relates the adsorbate and adsorbent - in this case toluene and GAC - to the equilibrium concentration of the adsorbate in water. To create an isotherm for Filtrasorb 400, a procedure similar to the GAC comparison test was conducted, the only difference being GAC amount as the independent variable instead of GAC type. Again, GAC was added to 200 mL serum bottles, which were filled with 10 mg/L toluene in Milli-Q water, capped with no headspace, and allowed to shake at 30°C for 24 hours at 250 rpm. Supernatant from the samples was filtered through 0.45 µm glass-fiber filters before running SPME and GC analysis. Samples were run in duplicates to determine precision, and controls with no GAC were also tested to account for other losses. **Table 13** lists the various GAC amounts used in this test and their average removal efficiencies against a starting toluene concentration of 10 mg/L and against the control.

***Table 13**: Filtrasorb 400 toluene removal efficiencies*

Sample	Removal	Removal from Control
Control (no GAC)	6.2±0.0%	0.0±0.0%
100mg	99.2±0.2%	99.1±0.2%
200mg	99.7±0.1%	99.7±0.1%
500mg	99.95±0.0%	99.9±0.0%
800mg	99.97±0.0%	99.97±0.0%
1000mg	99.97±0.0%	99.97±0.0%

There are many ways to relate the resulting values in a sorption isotherm, but the two most common models are by Freundlich and Langmuir (EPA 2019).

4.2.1.1 Freundlich Model

The Freundlich equation is as follows:

$$q_e = KC_e^{1/n}$$

where:

q_e = equilibrium loading on the GAC (mg chemical/g GAC)

K = adsorption capacity at unit concentration (mg/g)(L/mg)$^{1/n}$

C_e = equilibrium concentration in the water (mg chemical/L)

$1/n$ = strength of adsorption (unitless)

This equation can be linearized for graphing purposes by using logarithmic functions as follows:

$$\log q_e = \log K + \frac{1}{n} * \log C_e$$

Using the linearized Freundlich equation, the results are shown in **Figure 15**. A linear regression with an R^2 value of 0.983 indicates good correlation to the model (Nau 2018).

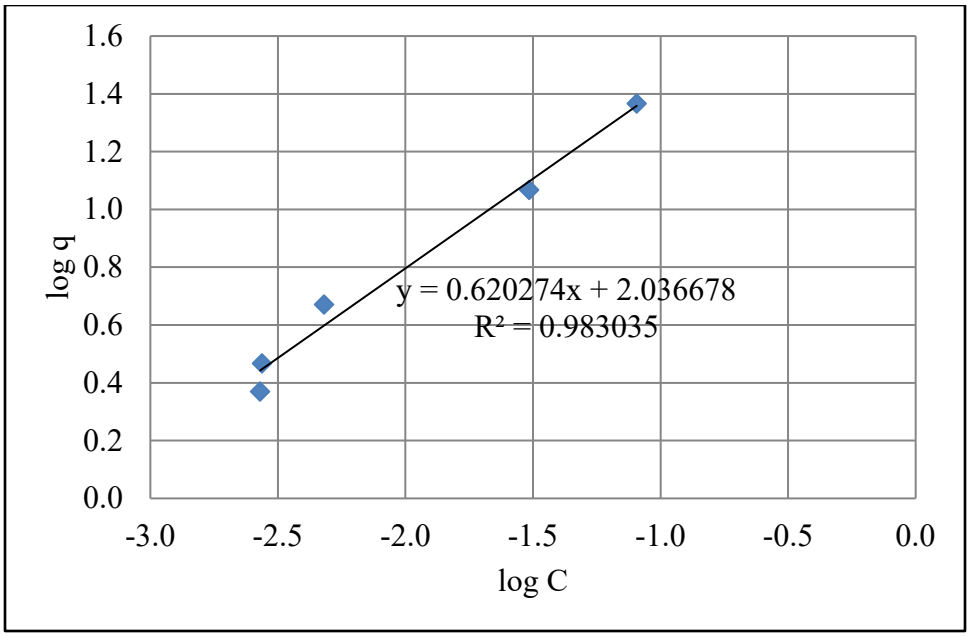

***Figure 15**: Freundlich model of Filtrasorb 400 sorption isotherm*

4.2.1.2 Langmuir Model

The Langmuir model has an equation as follows:

$$q_e = (q_{max} b C_e)/(1 + bC_e)$$

where:

q_e = equilibrium loading on the GAC (mg chemical/g GAC)

q_{max} = ultimate adsorption capacity (mg chemical/g GAC)

b = relative energy of adsorption (L/mg)

C_e = equilibrium concentration in the water (mg chemical/L)

Similar to the Freundlich equation, the Langmuir model can be linearized with inverse functions:

$$\frac{1}{q_e} = \frac{1}{q_{max} b C_e} + \frac{1}{q_{max}}$$

Using the linearized Langmuir equation, the results for the various GAC amounts are shown in **Figure 16**. A linear regression with an R^2 value above 0.96 indicates good correlation to the model (Nau 2018).

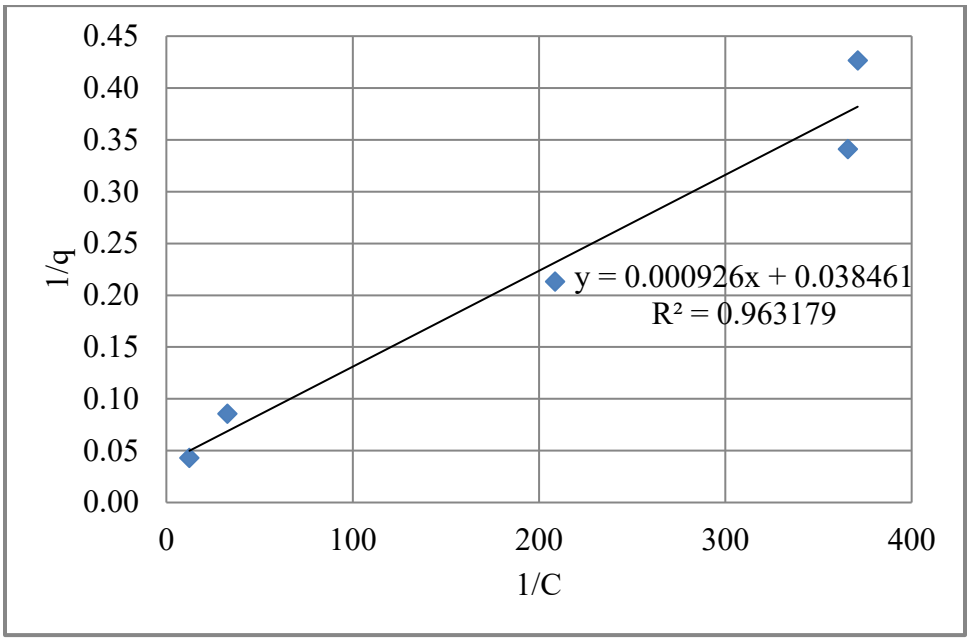

***Figure 16**: Langmuir model of Filtrasorb 400 sorption isotherm*

In comparing the two models, the R^2 value for the Langmuir model was less than that of the Freundlich model. Therefore, the Freundlich model more accurately describes the adsorptive capacity of Filtrasorb 400 for toluene removal. Using the Freundlich isotherm, the adsorptive capacity of Filtrasorb 400 was found to be 454 mg toluene/g GAC for GAC in a column in equilibrium with an influent toluene concentration of 10 mg/L.

4.3 Phase I: Acclimation and Biofilm Attachment

Inoculation of the reactors with UASB granular seed sludge occurred in August 2018 followed by an initial acclimation phase of no toluene feeding for approximately 150 days during which time continuous testing was done to monitor biological activity and performance.

4.3.1 Chemical and Solids Analysis Results

During acclimation, COD testing was conducted twice weekly to monitor biological activity. Results are shown in **Figure 17**. The BIO-GAC reactor performed well with a steady COD removal of around 80% for the entirety of the acclimation period. The BIO reactor, operated with UASB granular sludge only (no GAC), took a longer time to reach steady-state conditions.

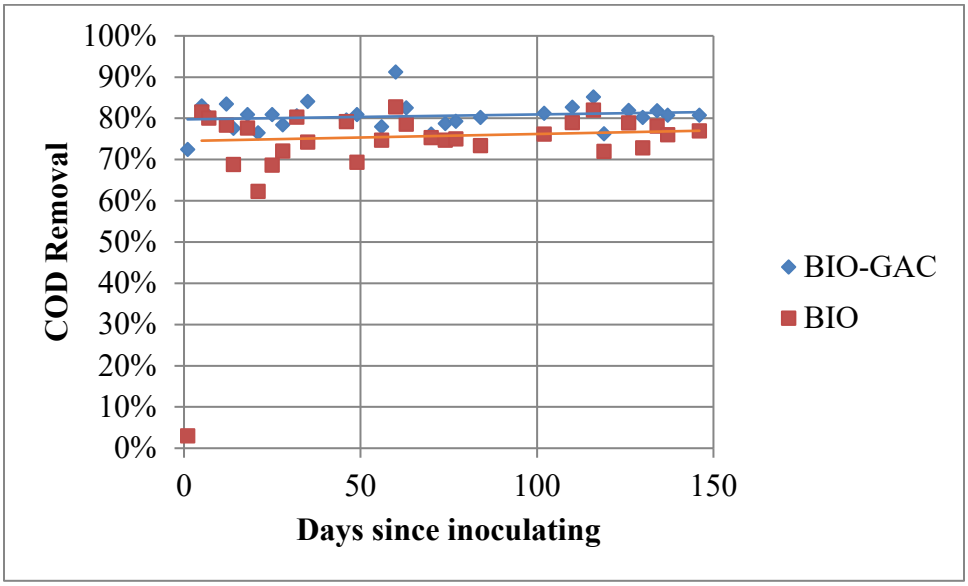

***Figure 17**: COD removal during acclimation phase I*

Effluent suspended solids (ESS) and effluent volatile suspended solids (EVSS) were also determined twice weekly to account for biomass loss in the system. Results are shown in **Figure 18** and **Figure 19**, respectively. Effluent suspended solids in the BIO reactor started out high, most likely from initial upflow disturbance. As the system acclimated to new conditions, the granules

grew in size, which allowed for a higher settling velocity and caused the effluent suspended solids to decrease. Suspended solids results in the BIO-GAC reactor effluent were consistent with a majority of samples having less than 50 mg/L ESS and EVSS. A mechanical error in the recycle pump of the BIO-GAC reactor caused the spikes in both ESS and EVSS on days 130 and 146.

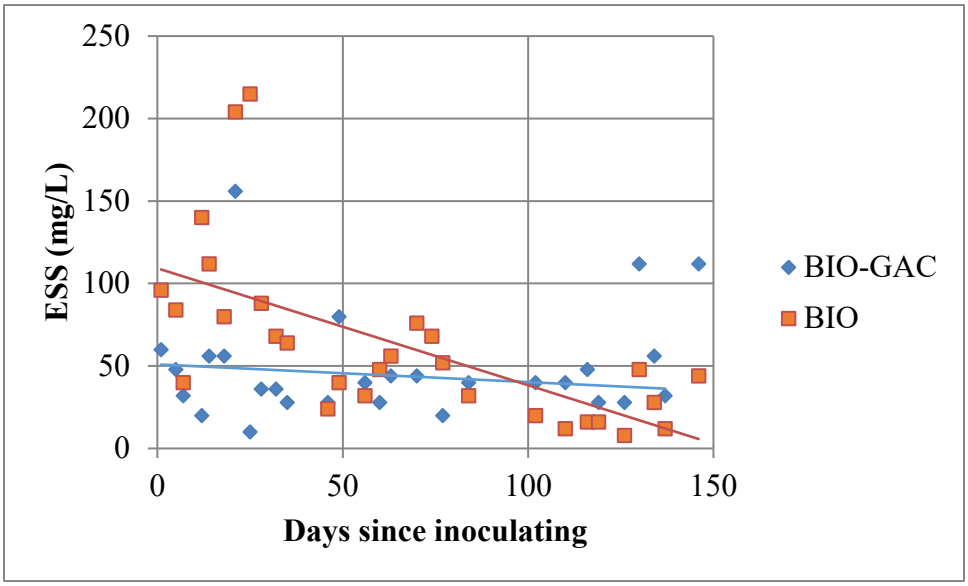

***Figure 18**: Effluent suspended solids during acclimation phase I*

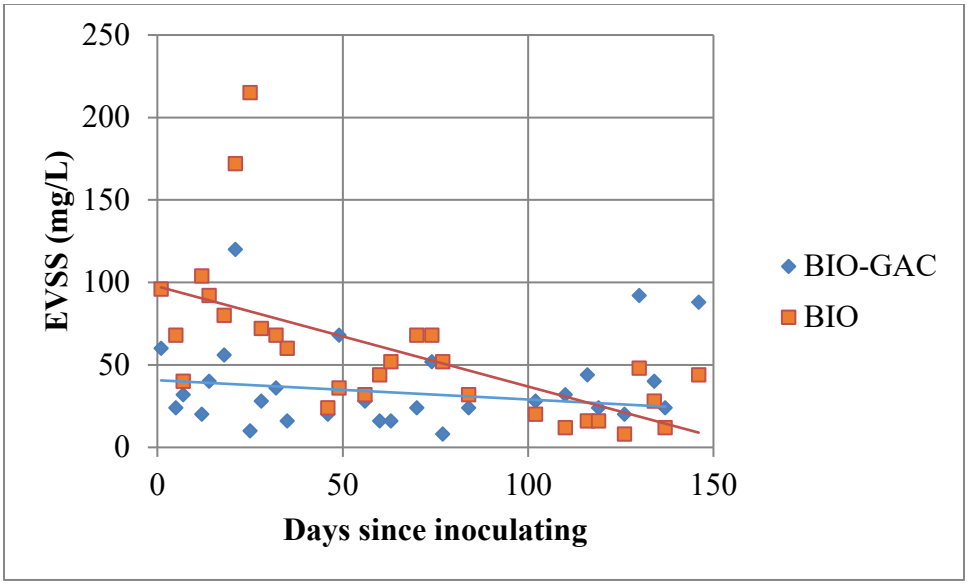

***Figure 19**: Effluent volatile suspended solids during acclimation phase I*

4.3.2 DNA Quantification Results

Because representative MLSS samples were difficult to obtain in the sealed UASB reactors, DNA quantification was used to measure biomass growth. Samples from the sludge bed of each reactor were taken and put through PowerBead DNA extraction and Qubit High Sensitivity analysis for quantification as described in Section 3.4 DNA Quantification. **Figure 20** shows the biological growth in both reactors in the first 50 days after initial startup. It is evident that growth began rapidly in both reactors before reaching a plateau. This indicates good conditions for bacteria in the reactors. Additionally, bed depth in both reactors visibly increased in both reactors over time, indicating continuous biological growth. It is important to note that although these DNA results show evidence for bacterial growth, it not an indicator of biofilm attachment in the BIO-GAC reactor. This is because the DNA quantification accounted for all DNA in a sample, including that from biofilm on GAC particles and from suspended flocs.

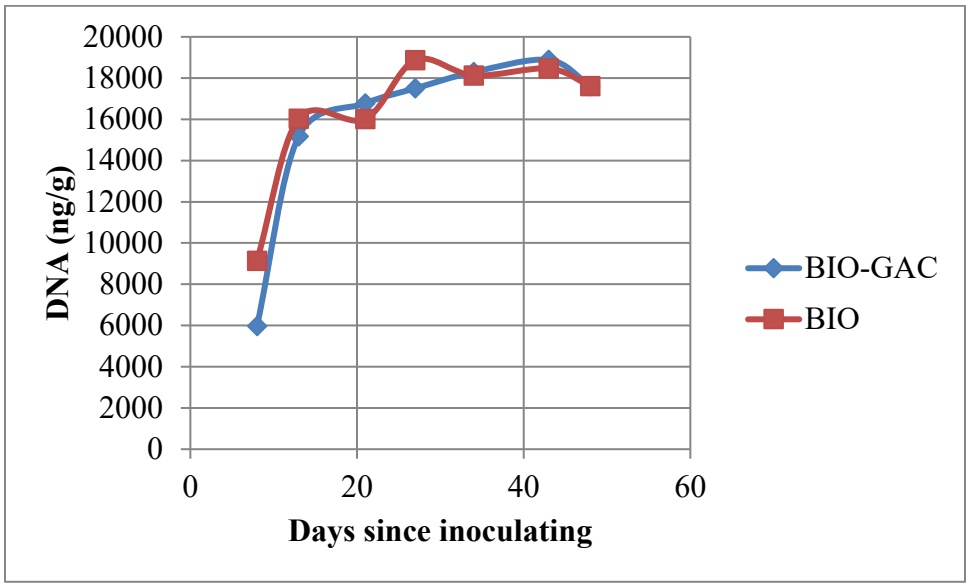

***Figure 20**: Biological growth during acclimation period*

4.3.3 Scanning Electron Microscopy Images

Mixed liquor samples were taken on days 60 and 120 after inoculation for SEM imaging. A fresh, unused Filtrasorb 400 GAC particle was also imaged under the same conditions as the reactor samples as a control. **Figure 21** shows imaging results for all samples. The fresh, unused GAC particle (**Figure 21a**) has sharp, jagged edges indicating no bacterial growth. By contrast, both the anaerobic granules and the BIO-GAC reactor particles (**Figure 21b-e**) have curved edges with visible bacterial growth. Additionally, the images show similar bacterial growth as those from Jamali et al. (2016), shown in **Figure 22**. These results provide clear evidence of consistent biofilm attachment on GAC particles from the BIO-GAC reactor after 60 and 120 days.

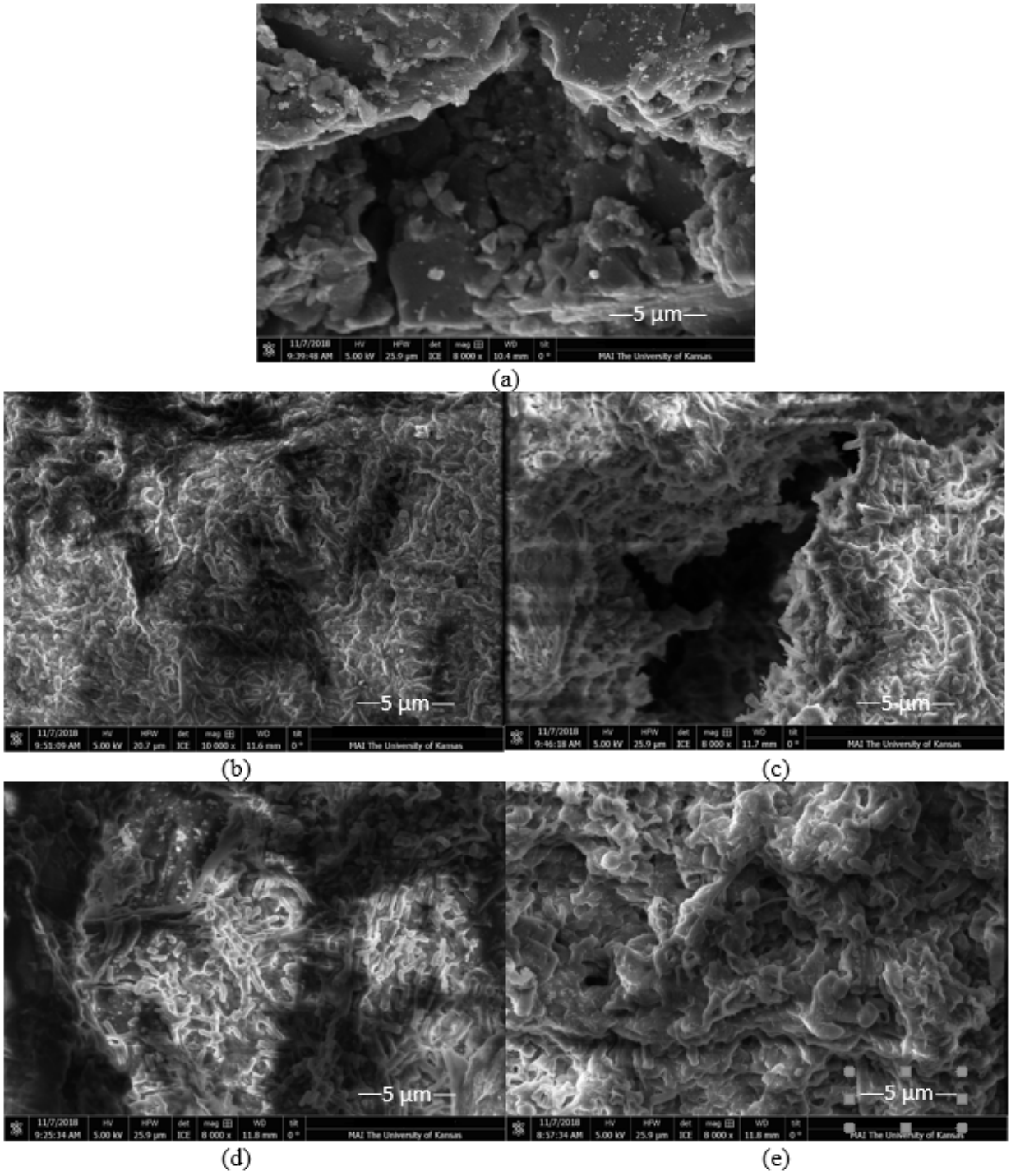

Figure 21*: SEM images of (a) fresh unused Fitlrasorb 400 GAC particle, (b,c) biofilm attachment on GAC particle from BIO-GAC reactor after 60 days and 120 days, and (d,e) anaerobic granule from BIO reactor after 60 days and 120 days, respectively*

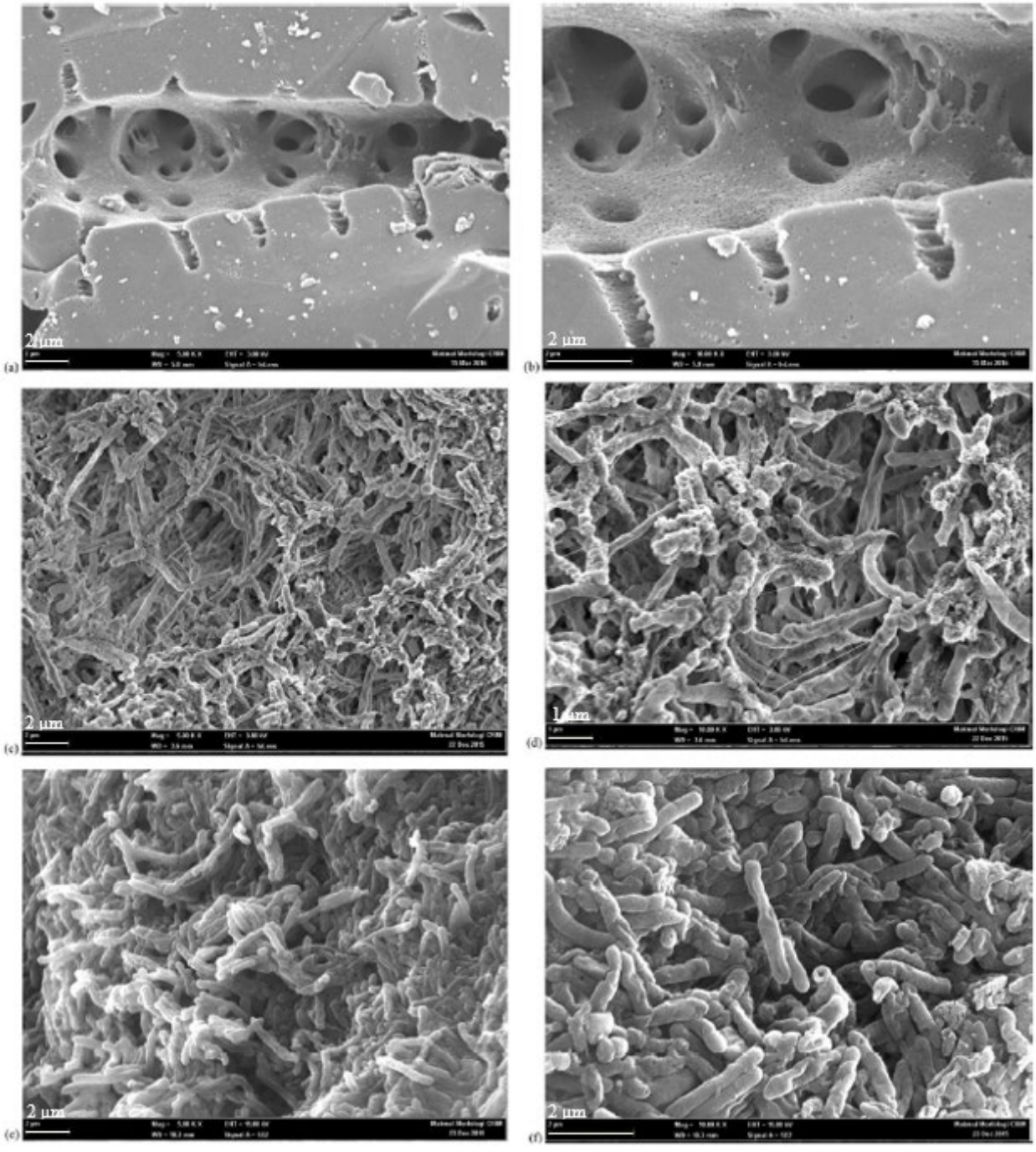

***Figure 22**: SEM images of (a,b) clean coconut shell GAC, (c,d) biofilm attachment on GAC particles, and (e,f) suspended cell (no carrier) at 5000x magnification and 10,000x magnification, respectively from Jamali et al. (2016)*

4.4 Phase II: Comparison of Anaerobic Granules and Biofilm on Granular Activated Carbon for Toluene Removal

The second phase of the experiment was active for two months and consisted of feeding toluene to both reactors at a concentration of 10 mg/L. The synthetic produced water composition remained the same as in phase I with the exception of a decreased glucose content from 1.22 g/L to 1.19 g/L to account for the additional carbon from toluene and maintain an equivalent COD feed of 1300 mg/L.

4.4.1 Chemical and Solids Analysis Results

COD testing continued twice weekly during phase II. Results are shown in **Figure 23**. Both rectors continued to perform well after introduction of toluene to the system.

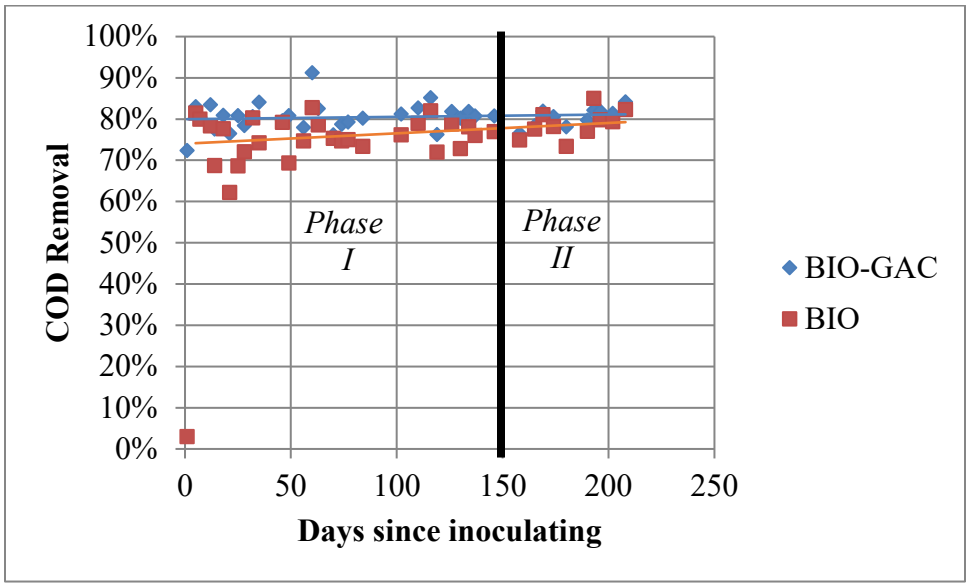

***Figure 23**: COD removal during phases I and II*

Effluent suspended solids and effluent volatile suspended solids testing was also continued twice weekly during phase II. Results are shown in **Figure 24** and **Figure 25**, respectively.

Suspended solids in both reactors remained under 50 mg/L with minimal change from the end of Phase I operation.

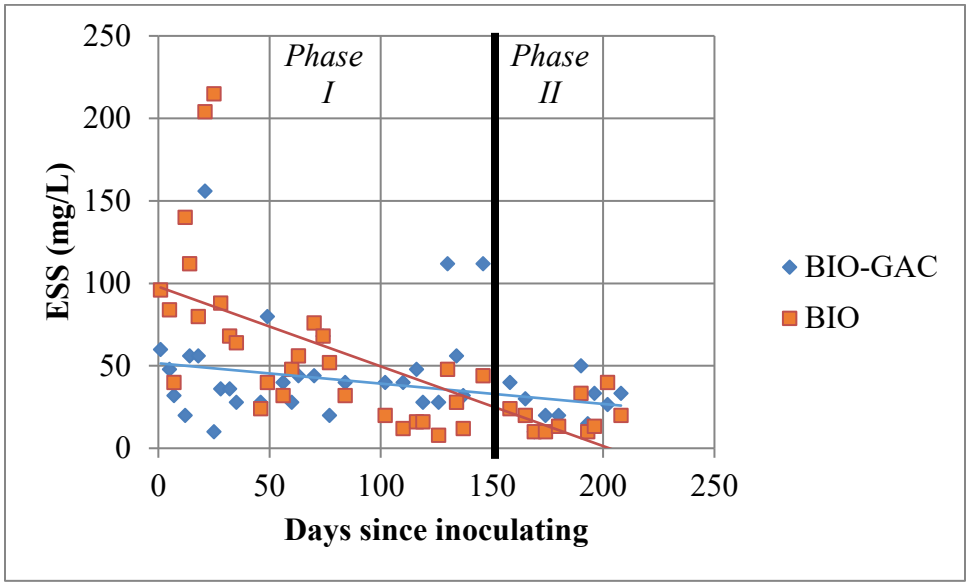

***Figure 24**: Effluent suspended solids during phases I and II*

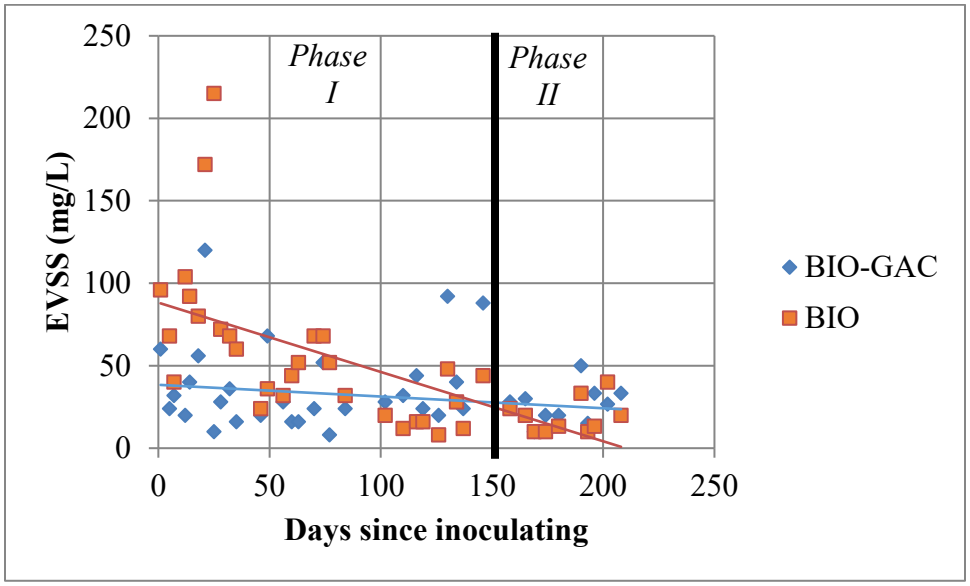

***Figure 25**: Effluent volatile suspended solids during phases I and II*

4.4.2 Toluene Removal Efficiency

Reactor performance was assessed by comparing toluene removal efficiencies. Effluent samples were taken weekly and evaluated using the SPME and GC analysis outlined in Section 3.6 Toluene Measurements. **Table 14** lists toluene measurements in the influent and effluent of both rectors in addition to their respective removal efficiencies. Throughout phase II, toluene concentrations from the BIO-GAC reactor were below the 0.90 µg/L MDL, representing greater than 99.9% removal in the system. However, toluene levels above 2 mg/L were detected in all samples taken from the BIO reactor at the same time intervals, with removal efficiency averaging 73.2±8.1% and reaching a maximum 86.5%. This supports the hypothesis that GAC provides additional support to reduce concentrations of soluble hydrocarbons like toluene in produced water.

***Table 14**: Toluene removal during phase II*

		BIO-GAC Reactor		BIO Reactor	
Days since start of phase II	**Influent toluene (mg/L)**	**Effluent toluene (mg/L)**	**Toluene removal**	**Effluent toluene (mg/L)**	**Toluene removal**
6	13.65	ND	>99.9%	3.11	77.2%
9	15.54	ND	>99.9%	3.30	78.8%
13	12.36	ND	>99.9%	3.58	71.0%
17	14.01	ND	>99.9%	4.17	70.3%
22	10.44	ND	>99.9%	4.09	60.9%
28	8.41	ND	>99.9%	3.22	61.6%
31	11.99	ND	>99.9%	3.31	72.4%
41	8.64	ND	>99.9%	2.60	69.9%
44	11.40	ND	>99.9%	3.11	72.7%
50	14.98	ND	>99.9%	2.03	86.5%
56	15.36	ND	>99.9%	2.42	84.3%

4.5 Phase III: Effect of Salinity on Toluene Removal

As discussed in Section 2.1.1 Constituents, salinity can be a large component of oil and gas produced water. To make a final conclusion on the ability of a BIO-GAC system to remove toluene, a third phase was conducted. Salinity was increased incrementally by 1% on a weekly basis starting at 1% and ending at 3%. During phase III, the toluene feeding target remained at 10 mg/L.

4.5.1 Chemical and Solids Analysis Results

COD results for the entirety of the experiment including phase III are shown in **Figure 26**. Both rectors continued to perform well after introduction of salinity to the system with COD removal efficiencies of around 80% each.

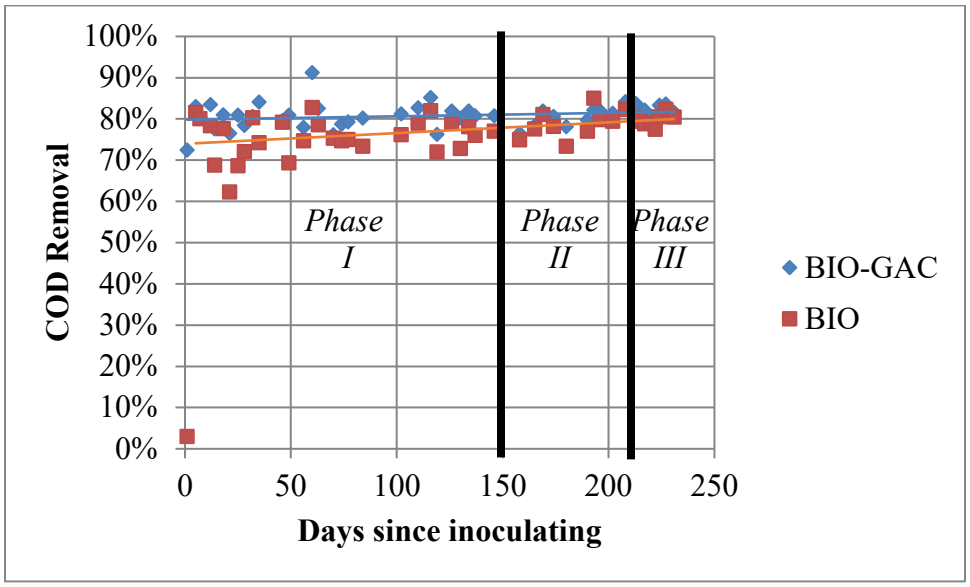

***Figure 26**: COD removal during phases I, II, and III*

ESS and EVSS results are shown in **Figure 27** and **Figure 28**, respectively. As in phase II, ESS and EVSS remained below 50 mg/L for both reactors indicating continued structural integrity of granule particles in the system.

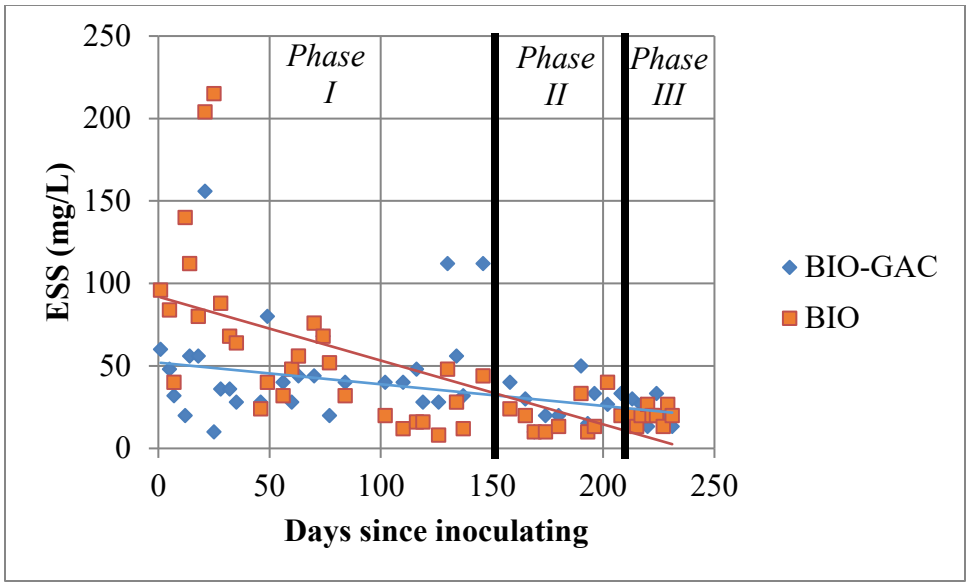

***Figure 27**: Effluent suspended solids during phases I, II, and III*

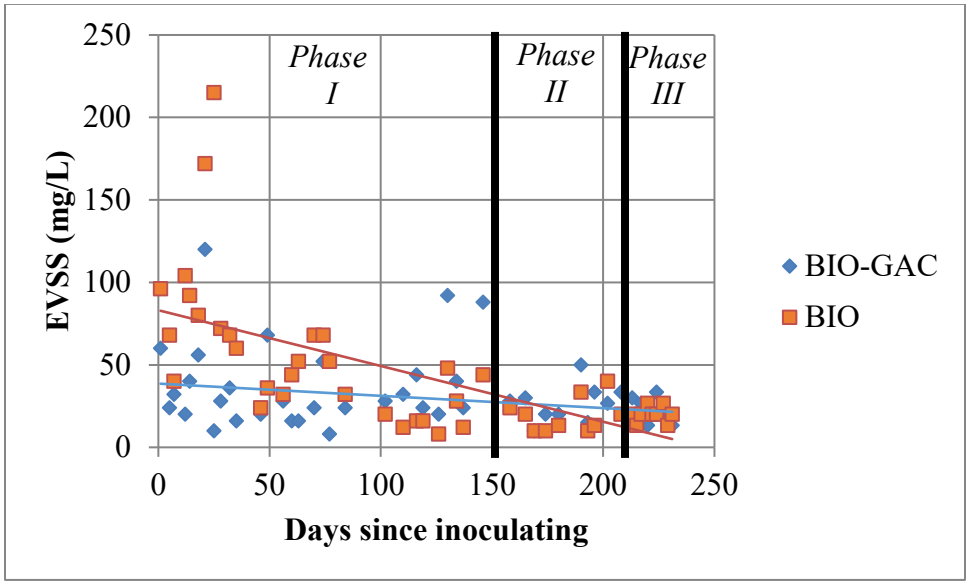

***Figure 28**: Effluent volatile suspended solids during phases I, II, and III*

4.5.2 Toluene Removal Efficiency

Toluene removal continued to be measured weekly by SPME and GC analysis. Results during phase III are shown in **Table 15**. The BIO-GAC reactor continued to outperform the BIO

reactor. Furthermore, the toluene concentrations in all BIO-GAC effluent samples continued to be below the 0.90 µg/L MDL. A decline in performance of the BIO reactor, however, was evident as the average toluene removal efficiency at each percent increment decreased from 85.5±2.8% to 64.2±7.0% and finally 35.1±25.4%.

***Table 15**: Toluene removal during phase III*

			BIO-GAC Reactor		BIO Reactor		
Salinity	**Days since start of phase III**	**Influent toluene (mg/L)**	**Effluent toluene (mg/L)**	**Toluene removal**	**Effluent toluene (mg/L)**	**Toluene removal**	**Average toluene removal**
1%	1	7.95	ND	>99.9%	1.40	82.4%	85.5±2.8%
	3	9.41	ND	>99.9%	1.32	86.0%	
	5	13.53	ND	>99.9%	1.63	88.0%	
2%	8	10.70	ND	>99.9%	3.02	71.8%	64.2±7.0%
	10	14.91	ND	>99.9%	5.58	62.6%	
	12	18.03	ND	>99.9%	7.55	58.1%	
3%	15	9.60	ND	>99.9%	3.42	64.3%	35.1±25.4%
	17	10.88	ND	>99.9%	8.88	18.4%	
	19	7.93	ND	>99.9%	6.14	22.5%	

The decline in BIO reactor performance can be seen visually in **Figure 29**, which shows the progression of toluene removal efficiencies throughout phases II and III. Adding salinity at 1% to the system did not decrease the toluene removal efficiency of either reactor. In phase III, however, there are sudden decreases in toluene removal in the BIO reactor immediately following a stepwise salinity increase to both 2% and 3% indicating a shock to bacteria. The largest loss of 45.9% removal efficiency came two days after increasing salinity to 3%. It would be beneficial in future experimentation to continue to raise salinity to analyze its effects on both reactors' performance. As mentioned in Section 2.1.1 Constituents, TDS in produced water can reach up to 400,000 mg/L, equal to 40% salinity.

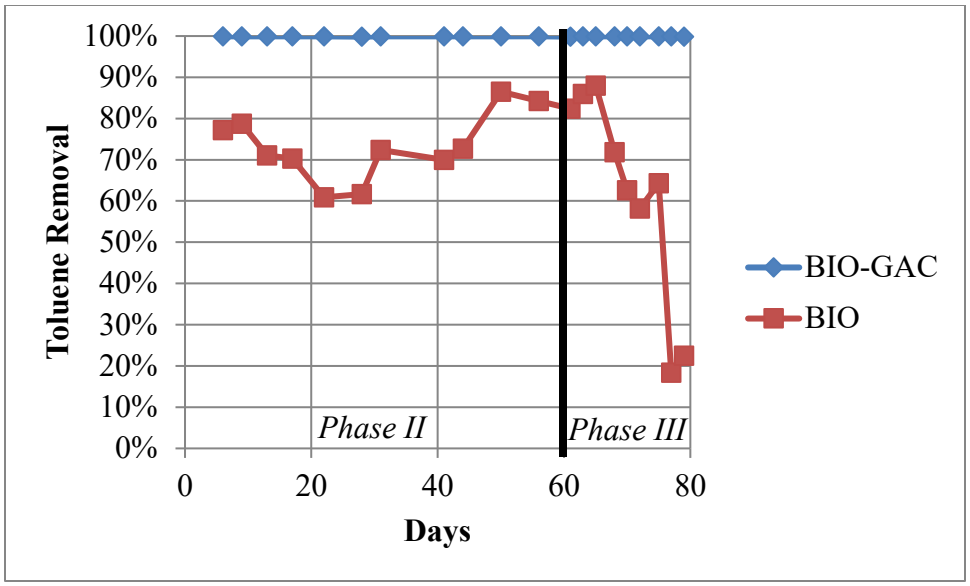

***Figure 29**: Toluene removal during phases II and III*

4.6 Statistical Analysis and Experimental Summary

Two-tailed statistical t-tests for sample means with unequal variance and a 95% confidence interval (α=0.05) were used to compare toluene removal results. Ten tests were conducted comparing performance between the BIO-GAC and BIO reactors and between salinity levels in each reactor. Resulting p-values for each t-test are shown in **Table 15** with labels G0-G3 and B0-B3 representing the BIO-GAC (G) or BIO reactor (B) at 0-3% salinity. If the p-value is below 0.05, the two sample means are considered significantly different. A statistical conclusion designating the sample means as different or similar based on the p-value is also listed in **Table 16** for each t-test.

***Table 16**: Statistical t-test results comparing toluene removal results*

Test between BIO-GAC & BIO	p-value	statistical conclusion	Effect of salinity on BIO-GAC performance	p-value	statistical conclusion	Effect of salinity on BIO performance	p-value	statistical conclusion
G0-B0	0.0000	DIFFERENT	**G0-G1**	0.3360	SIMILAR	**B0-B1**	0.0019	DIFFERENT
G1-B1	0.0126	DIFFERENT	**G1-G2**	0.6297	SIMILAR	**B1-B2**	0.0163	DIFFERENT
G2-B2	0.0125	DIFFERENT	**G2-G3**	0.4226	SIMILAR	**B2-B3**	0.1958	SIMILAR
G3-B3	0.0475	DIFFERENT						

It is clear from the results there is significant difference between the BIO-GAC reactor and BIO reactor (G0-B0, G1-B1, G2-B2, and G3-B3) throughout the duration of the experiment. This further supports the hypothesis that GAC provides additional support to reduce toluene concentrations more than a biological system would alone. The t-test results for the BIO-GAC reactor (G0-G1, G1-G2, and G2-G3) also indicate salinity up to 3% had no effect on reactor performance. As indicated above, BIO-GAC effluent toluene concentrations remained under the 0.90 µg/L MDL for the entirety of the experiment. Future research on the performance of the BIO-GAC reactor at higher salinity to reflect real produced water values should be conducted to determine if there is a point at which toluene removal is affected. The BIO reactor, on the other hand, showed significant difference in two of its tests: between no salinity and 1% salinity (B0-B1), and between 1% and 2% salinity (B1-B2). It can be concluded that salinity had a significant effect on reactor performance. No statistical difference was detected between the BIO reactor at 2% and 3% salinity (B2-B3). However, as mentioned above, the largest decline in toluene removal efficiency occurred during this phase of operation and it is possible that more samples at this level would result in a significant difference.

The results of this experimentation show that the BIO-GAC system is an effective treatment for toluene removal from produced water. This conclusion matches findings from the

literature. Estrada-Arriaga et al. (2012) published similar results for an anaerobic BIO-GAC system that removed >99.9% toluene while maintaining 85% COD removal. A study focused on BTEX removal also reported 95.6-99.9% toluene for a BIO-GAC system (Zhang et al. 2013). Based on these studies and others, BIO-GAC is a proven efficient treatment technology for toluene removal.

Results from this study further suggest that the BIO-GAC reactor has a higher toluene removal capacity than the BIO reactor. However, these results give little indication of the BIO-GAC reactor's toluene removal abilities compared to a system that utilizes GAC alone. As shown by the GAC comparison study in Section 4.1 Comparison of Granular Activated Carbon Types, >99% toluene removal was achieved in batch systems filled only with Filtrasorb 400 and toluene, indicating that a GAC system may exhibit the same high level of performance as the BIO-GAC reactor.

A case can be made for the BIO-GAC system over a GAC system based on the various constituents of produced water besides toluene that are unable to be effectively treated by physical adsorption alone. For example, Mancini et al. (2017) reported a maximum COD removal of 26% in a GAC filtration system. Furthermore, a comparison of BIO-GAC and GAC systems by Xing et al. (2008) showed that BIO-GAC was able to remove 96% of DOC compared to a GAC system that removed 54%. Moreover, Scott et al. (1995) demonstrated that although GAC generally has a low adsorptive capacity for heavy metals, a BIO-GAC system can enhance metal uptake from aqueous waste. Not only is BIO-GAC superior in targeting multiple constituents, it would also allow the industry to cut costs and necessary space by replacing multiple treatment steps with one system. Between the three processes, BIO-GAC is the optimal system for produced water

treatment because it can effectively remove toluene and other adsorbable constituents in addition to constituents that are best removed with biological treatment.

4.7 Toluene Removal Pathway

There are three potential removal pathways for toluene in the UASB reactor system: volatilization, adsorption, and biological degradation. It is difficult to determine which of the three is responsible for toluene removal from the aqueous phase in this system because it is sealed for safety as discussed in Section 3.7 Safety. However, there are ways to make a reasonable conclusion as to which pathway is most likely. As toluene is a highly volatile compound, some volatilization is expected to occur. To minimize uncertainty due to volatilization in removal calculations, reactor effluent results were compared to influent samples taken at the same time interval.

Distinguishing between adsorption and biological degradation is more challenging. It is clear from the GAC comparison tests and sorption isotherm that GAC has a high adsorptive capacity for toluene. The BIO-GAC reactor was also found to be significantly better than the BIO reactor at removing toluene. These findings indicate that adsorption occurred in the BIO-GAC reactor but does not indicate how much. One could theoretically quantify the toluene adsorbed or biologically degraded by simply calculating the difference between the BIO-GAC and BIO reactors. However, there is likely to be adsorption via biosorption onto anaerobic granules present in the BIO reactor, therefore this calculation would be inappropriate. Additionally, adsorption lowers toluene concentration in solution, such that the substrate concentration available for biodegradation will be much lower in the BIO-GAC reactor compared to the BIO reactor.

SPME and GC analysis is a more appropriate method to identify and quantify derivatives of toluene degradation. **Figure 30** shows the anaerobic biological degradation pathway of toluene including its intermediate forms. Using a scan method on the GC, a chromatogram shows potential intermediate degradation products in addition to toluene. One such chromatogram is shown in **Figure 31**. Scan GC chromatograms were made for all phase II and phase III experimental samples. While peaks in addition to toluene were found in some samples, they were either unable to be identified with high confidence or they were determined to be resultants of the synthetic produced water matrix. No anaerobic toluene degradation derivatives were identified in any of the samples, therefore the extent of biological degradation cannot be concluded with this method. Nevertheless, it has been shown here that there is additional toluene adsorption achieved by the GAC particles that is unable to be performed by the microbes alone. Future research to distinguish between adsorption and biological degradation in the BIO-GAC reactor system is necessary. A method that involves taking biomass from the BIO-GAC reactor and fixing the granules to determine its toluene removal when bacteria is no longer active is recommended.

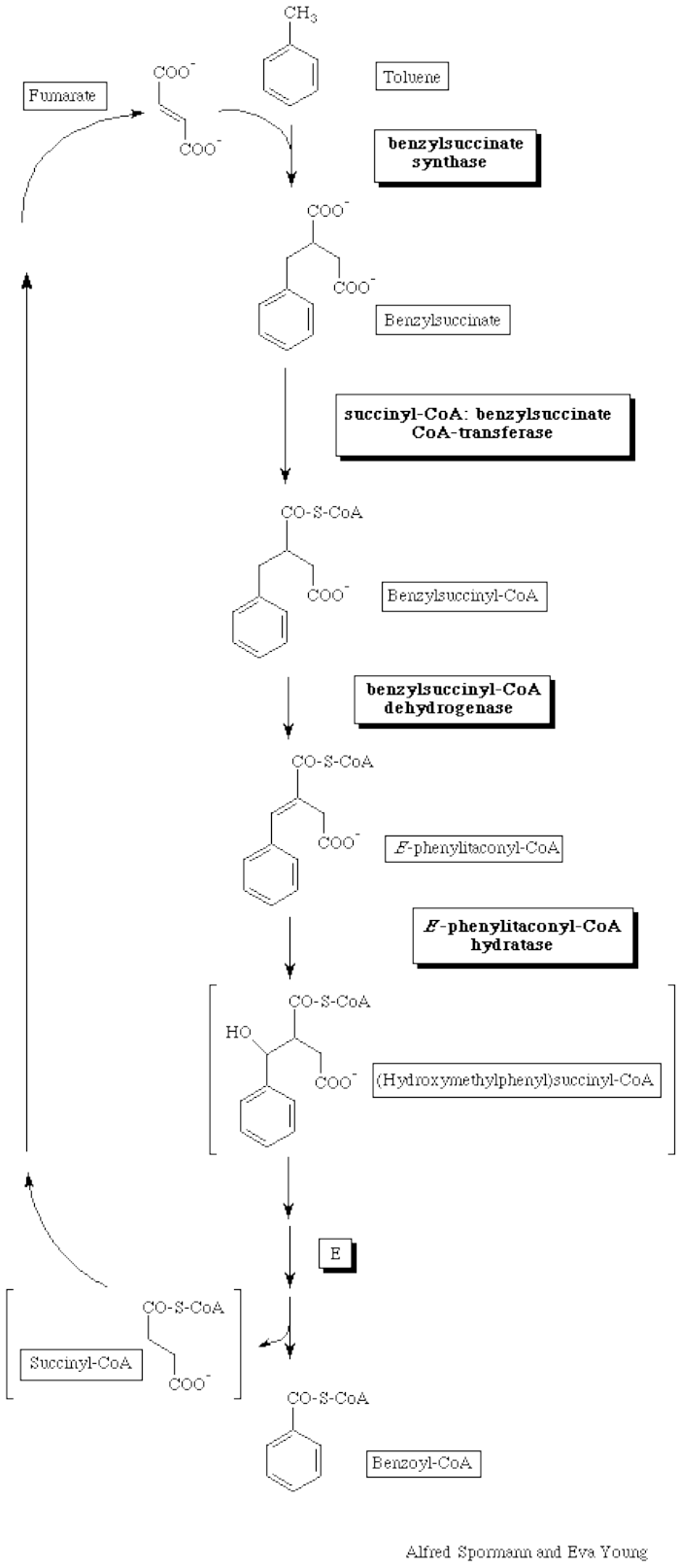

***Figure 30**: Anaerobic toluene degradation pathway*

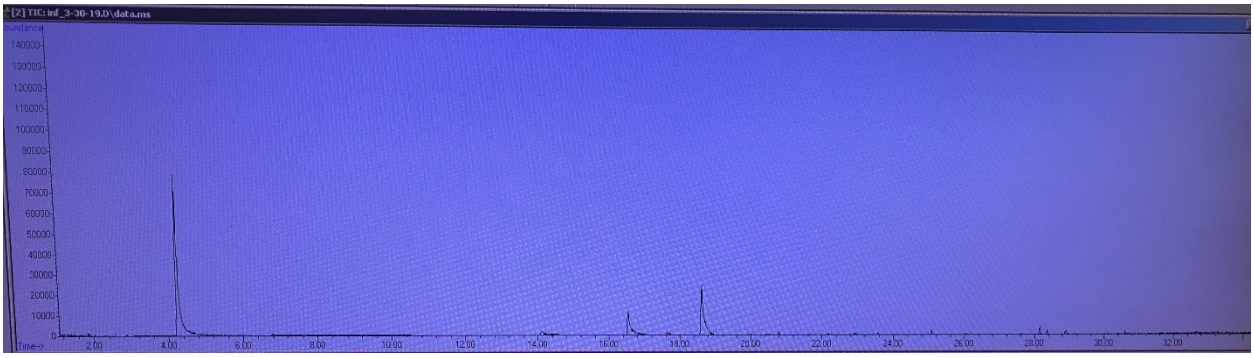

***Figure 31**: Chromatogram of March 30, 2019 influent sample using scan GC method*

5.0 Conclusions

The need for new treatment systems for oil and gas produced water in the United States is increasing as production companies look for new ways to dispose of this waste stream. Produced water has a variety of constituents that are not easily treated by conventional systems, among them aromatic hydrocarbons such as toluene.

This study aimed to evaluate a BIO-GAC system for toluene removal from produced water and assess its performance under hypersaline conditions commonly found in produced water. This was achieved by operation of two lab-scale UASB reactors, a BIO-GAC reactor and a BIO reactor. Biofilm attachment on GAC particles in the BIO-GAC reactor was confirmed by SEM imaging after 60 and 120 days. Both reactors reached steady COD removal rates around 80% in the acclimation phase I.

After 150 days, toluene at 10 mg/L was added in the synthetic produced water fed to both reactors to begin phase II. During this time, toluene removal in the BIO-GAC reactor was consistently >99.9%, and removal in the BIO reactor averaged 73.2±8.1%. A student t-test showed there was significant difference between the two reactors, conclusively showing higher performance in the BIO-GAC system.

Phase III began on day 210 when 1% salinity was added to the influent synthetic produced water for both reactors. Salinity was subsequently increased by 1% every 7 days until 3% salinity was reached. Under these conditions, the BIO-GAC reactor continued to perform at a toluene removal rate of >99.9% throughout phase III. At 1% salinity, the BIO reactor exhibited 85.5±2.8% toluene removal. However, BIO reactor performance declined in the weeks following; efficiencies were 64.2±7.0% and 35.1±25.4% at 2% and 3% salinity, respectively. This indicates that salinity

did affect toluene removal in the BIO reactor. Statistical analysis by student t-tests also determined results between both reactors were significantly different. Phase III demonstrated BIO-GAC's resistance to hypersaline shock and provided understanding of the effects of salinity on toluene removal in a BIO system.

Although processes that utilize GAC alone may exhibit equally high toluene removal rates, BIO-GAC has the ability to effectively remove other constituents in produced water that are unable to be treated by GAC systems. Throughout experimentation, the BIO-GAC removed COD at a steady rate around 80% while removing high levels of toluene, and literature shows some GAC systems do not have high levels of COD removal. Other studies show higher DOC and heavy metal removal rates in BIO-GAC, both of which are common in produced water. In conclusion, BIO-GAC systems can provide a more comprehensive approach to produced water treatment by targeting multiple contaminants at once.

The findings of this study provide a detailed analysis of a BIO-GAC system for toluene removal from produced water. This research begins to fill a gap in literature on the effects of salinity on this treatment process and prompts a much needed discussion on developing technologies easily adoptable by the produced water industry.

5.1 Future Directions

For future studies on BIO-GAC, it is important to study toluene removal at higher salinity levels. Produced water across the US has a wide range of salinity and TDS levels can reach up to 400,000 mg/L, or 40% salinity. Additionally, identifying the toluene removal mechanism is essential to understanding and developing new treatment technologies. Therefore, further research is necessary to explore these areas and broaden knowledge of BIO-GAC systems.

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Appendices

Appendix A – SIM Method for SPME/GC analysis

```
                                    acqmeth.txt
              INSTRUMENT CONTROL PARAMETERS:    Agilent 5977A GCMS
              ==========================================================

   D:\MassHunter\GCMS\1\methods\toluene-split-SIM-SPME 1-30-18-.M
      Fri Mar 29 14:34:43 2019

Control Information
------- -----------

Sample Inlet              : GC
Injection Source          : Manual
Mass Spectrometer         : Enabled


 No Sample Prep method has been assigned to this method.


GC
Oven
Temperature
Setpoint                                          On
(Initial)                                         35 °C
Hold Time                                         12 min
Post Run                                          40 °C
Program
#1 Rate                                           8 °C/min
#1 Value                                          150 °C
#1 Hold Time                                      2 min


Equilibration Time                                1 min
Max Temperature                                   325 °C
Maximum Temperature Override                      Disabled
Slow Fan                                          Disabled
Cryo                                              Off

ALS
Sample Overlap
Mode                                              Sample overlap is not enabled

ALS Errors                                        Pause for user interaction

Front SS Inlet He
Mode                                              Split
Heater                                            On    280 °C
Pressure                                          On    11.604 psi
Total Flow                                        On    33.5 mL/min
Septum Purge Flow                                 On    2 mL/min
Gas Saver                                         On    20 After 10 min mL/min
Split Ratio                                       20 :1
Split Flow                                        30 mL/min
Liner                                             Agilent 5181-3316: 900 µL (Splitless,
single taper liner, deacti)

Thermal Aux 2 (MSD Transfer Line)
Temperature
Setpoint                                          On
(Initial)                                         250 °C
Post Run                                          0 °C


Column
Column #1
```

```
Flow
Setpoint                                        Off
(Initial)                                       1.5 mL/min
Post Run                                        1.5 mL/min

Agilent 19091S-433UI
HP-5ms Ultra Inert
0 °C-325 °C (350 °C): 30 m x 250 µm x 0.25 µm
Column lock                                     Unlocked
In                                              Front SS Inlet He
Out                                             MSD
(Initial)                                       35 °C
Pressure                                        11.604 psi
Flow                                            1.5 mL/min
Average Velocity                                44.297 cm/sec
Holdup Time                                     1.1287 min

Column Outlet Pressure                          0 psi

Signals
Signal #1:  Test Plot
Description                                     Test Plot
Details
Save                                            Off
Data Rate                                       50 Hz
Dual Injection Assignment                       Front Sample

Signal #2:  Test Plot
Description                                     Test Plot
Details
Save                                            Off
Data Rate                                       50 Hz
Dual Injection Assignment                       Back Sample

Signal #3:  Test Plot
Description                                     Test Plot
Details
Save                                            Off
Data Rate                                       50 Hz
Dual Injection Assignment                       Back Sample

Signal #4:  Test Plot
Description                                     Test Plot
Details
Save                                            Off
Data Rate                                       50 Hz
Dual Injection Assignment                       Back Sample



MS Information
-- -----------


General Information
------- -----------

Acquisistion Mode         : SIM
Solvent Delay (minutes)   : 1.00
Tune file                 : D:\MassHunter\GCMS\1\5977\atune.u
EM Setting mode Gain      : 1.000000
```

acqmeth.txt

```
Number of SIM Groups      : 1
Run Time (if MS only)     : 650 minutes

[SIM Parameters]
Group 1                Group ID                    : toluene
Resolution                 : 1
Group Start Time           : 1.00
Number of Ions             : 2
Ions
Dwell In Group             :(  Mass,  Dwell) (  Mass,  Dwell)  (  Mass,  Dwell)
                            (  91.00,100  )  (  92.00,100  )


[MSZones]

MS Source                    : 230 C   maximum 250 C
MS Quad                      : 150 C   maximum 200 C

Timed Events
----- ------
Number Events= 0


                    END OF MS ACQUISTION PARAMETERS

                      TUNE PARAMETERS for SN: US1345M203
                      ----------------------------------

 Trace Ion Detection is OFF.

 EMISSION     :      34.593
 ENERGY       :      70.007
 REPELLER     :      12.986
 IONFOCUS     :      90.331
 ENTRANCE_LE  :      12.582
 EMVOLTS      :    1629.372
                              Actual EMV :  1565.1
                              GAIN FACTOR :   1.00
 AMUGAIN      :    1990.000
 AMUOFFSET    :     121.938
 FILAMENT     :       1.000
 DCPOLARITY   :       1.000
 ENTLENSOFFS  :      10.611
 MASSGAIN     :    -182.000
 MASSOFFSET   :     -33.000

                      END OF TUNE PARAMETERS
                      ----------------------


                    END OF INSTRUMENT CONTROL PARAMETERS
                    ------------------------------------
```

Appendix B – Scan Method for SPME/GC Analysis

```
                                    acqmeth.txt
              INSTRUMENT CONTROL PARAMETERS:    Agilent 5977A GCMS
              ---------------------------------------------------

   D:\MassHunter\GCMS\1\methods\toluene-split-scan-SPME 3-30-19-.M
      Sun Mar 31 15:45:51 2019

Control Information
------- -----------

Sample Inlet                : GC
Injection Source            : Manual
Mass Spectrometer           : Enabled


 No Sample Prep method has been assigned to this method.


GC
Oven
Temperature
Setpoint                                        On
(Initial)                                       35 °C
Hold Time                                       8 min
Post Run                                        40 °C
Program
#1 Rate                                         8 °C/min
#1 Value                                        230 °C
#1 Hold Time                                    2 min


Equilibration Time                              1 min
Max Temperature                                 325 °C
Maximum Temperature Override                    Disabled
Slow Fan                                        Disabled
Cryo                                            Off

ALS
Sample Overlap
Mode                                            Sample overlap is not enabled

ALS Errors                                      Pause for user interaction

Front SS Inlet He
Mode                                            Split
Heater                                          On    280 °C
Pressure                                        On    11.604 psi
Total Flow                                      On    33.5 mL/min
Septum Purge Flow                               On    2 mL/min
Gas Saver                                       On    20 After 10 min mL/min
Split Ratio                                     20 :1
Split Flow                                      30 mL/min
Liner                                           Agilent 5181-3316: 900 µL (Splitless,
single taper liner, deacti)

Thermal Aux 2 (MSD Transfer Line)
Temperature
Setpoint                                        On
(Initial)                                       250 °C
Post Run                                        0 °C


Column
Column #1
```

```
Flow
Setpoint                                        Off
(Initial)                                       1.5 mL/min
Post Run                                        1.5 mL/min

Agilent 190915-433UI
HP-5ms Ultra Inert
0 °C-325 °C (350 °C): 30 m x 250 µm x 0.25 µm
Column lock                                     Unlocked
In                                              Front SS Inlet He
Out                                             MSD
(Initial)                                       35 °C
Pressure                                        11.604 psi
Flow                                            1.5 mL/min
Average Velocity                                44.297 cm/sec
Holdup Time                                     1.1287 min

Column Outlet Pressure                          0 psi

Signals
Signal #1:  Test Plot
Description                                     Test Plot
Details
Save                                            Off
Data Rate                                       50 Hz
Dual Injection Assignment                       Front Sample

Signal #2:  Test Plot
Description                                     Test Plot
Details
Save                                            Off
Data Rate                                       50 Hz
Dual Injection Assignment                       Back Sample

Signal #3:  Test Plot
Description                                     Test Plot
Details
Save                                            Off
Data Rate                                       50 Hz
Dual Injection Assignment                       Back Sample

Signal #4:  Test Plot
Description                                     Test Plot
Details
Save                                            Off
Data Rate                                       50 Hz
Dual Injection Assignment                       Back Sample



MS Information
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General Information
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Acquisistion Mode         : Scan
Solvent Delay (minutes)   : 1.00
Tune file                 : D:\MassHunter\GCMS\1\5977\atune.u
EM Setting mode Gain      : 1.000000
```

```
Normal or Fast Scanning  : Normal Scanning
Trace Ion Detection      : Off
Run Time (if MS only)    : 650 minutes

[Scan Parameters]
Start Time               : 1.00
Low Mass                 : 45.00
High Mass                : 600.00
Threshold                : 150
A/D Samples:             : 4


[MSZones]

MS Source                   : 230 C   maximum 250 C
MS Quad                     : 150 C   maximum 200 C

Timed Events
----- ------
Number Events= 0


                    END OF MS ACQUISTION PARAMETERS

                       TUNE PARAMETERS for SN: US1345M203
                       ----------------------------------

 Trace Ion Detection is OFF.

 EMISSION     :       34.593
 ENERGY       :       70.007
 REPELLER     :       12.986
 IONFOCUS     :       90.331
 ENTRANCE_LE  :       12.582
 EMVOLTS      :     1676.433
                                Actual EMV :  1568.8
                                GAIN FACTOR :   1.00
 AMUGAIN      :     1990.000
 AMUOFFSET    :      121.938
 FILAMENT     :        1.000
 DCPOLARITY   :        1.000
 ENTLENSOFFS  :       10.611
 MASSGAIN     :     -182.000
 MASSOFFSET   :      -33.000

                       END OF TUNE PARAMETERS
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                    END OF INSTRUMENT CONTROL PARAMETERS
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```